STIC Search Report
EIC 1700

STIC Database Tracking Number: 176451

TO: Ben Sackey
Location: REM 5B31
Art Unit : 1626
January 20, 2006

Case Serial Number: 10/736387

From: Kathleen Fuller
Location: EIC 1700
REMSEN 4B28
Phone: 571/272-2505
Kathleen.Fuller@uspto.gov

Search Notes

ACCESS DB # 176451

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Mrs Fuller

Scientific and Technical Information Center

SEARCH REQUEST FORM

Requester's Full Name: GEN SACKEY Examiner #: 73489 Date: 1/11/06

Art Unit: 1626 Phone Number: 2-0704 Serial Number: 10/736,357

Location (Bldg & room): REM 5B31 Mailbox #: ____ Results Format Preferred (circle): PAPER DISK

To ensure an efficient and quality search, please attach a copy of the cover sheet, claims, and abstract or fill out the following:

Title of Invention: Process for recovering acrylonitile or methacrylonitile

Inventors (please provide full names): Godbole et al.

SCIENTIFIC REFERENCE BR
Sci & Tech Inf - Ctr
JAN 12 REC'D
Pat & T.M. Office

Earliest Priority Date: 01/03/03

Search Topic:

Please provide a detailed statement of the search topic, and describe as specifically as possible the subject matter to be searched. Include the elected species or structures, keywords, synonyms, acronyms, and registry numbers, and combine with the concept or utility of the invention. Define any terms that may have a special meaning. Give examples or relevant citations, authors, etc., if known.

For Sequence Searches Only Please include all pertinent information (parent, child, divisional, or issued patent numbers) along with the appropriate serial number.

A process for preparing acrylonitile & methacrylonitile comprising contacting a gaseous effluent comprising nitrile monomer with an aqueous quench liquid in a first column, contacting the gaseous effluent from 1st column with H_2O in a 2nd column, forming a Soln of nitrile and co-products, subjecting Soln to H_2O extractive distillation in a recovery distillation column employing H_2O and collecting nitrile monomer and H_2O in an overhead decanter, then adding alkaline cmpd. eg. ammonium carbonate or bicarbonate or carbamate, alkaline diamines and mixtures thereof.

STAFF USE ONLY

Searcher: K. Fuller

Searcher Phone #: ____

Searcher Location: ____

Date Searcher Picked Up: ____

Date Completed: 1/20/06

Searcher Prep & Review Time: 40

Online Time: 40

Type of Search

____ NA Sequence (#)

____ AA Sequence (#)

2 Structure (#)

____ Bibliographic

____ Litigation

____ Fulltext

____ Other

Vendors and cost where applicable

✓ STN ____ Dialog

____ Questel/Orbit ____ Lexis/Nexis

____ Westlaw ____ WWW/Internet

____ In-house sequence systems

____ Commercial ____ Oligomer ____ Seqs Length

____ Interference ____ SPDI ____ Encode/Transl

____ Other (specify)

STIC Search Results Feedback Form

USPTO

EIC17000

Questions about the scope or the results of the search? Contact *the EIC searcher or contact:*

Kathleen Fuller, EIC 1700 Team Leader
571/272-2505 REMSEN 4B28

Voluntary Results Feedback Form

- *I am an examiner in Workgroup:* [ ] *Example: 1713*
- *Relevant prior art* ***found****, search results used as follows:*
  - ☐ 102 rejection
  - ☐ 103 rejection
  - ☐ Cited as being of interest.
  - ☐ Helped examiner better understand the invention.
  - ☐ Helped examiner better understand the state of the art in their technology.

  Types of relevant prior art found:
  - ☐ Foreign Patent(s)
  - ☐ Non-Patent Literature
    (journal articles, conference proceedings, new product announcements etc.)

- *Relevant prior art* ***not found:***
  - ☐ Results verified the lack of relevant prior art (helped determine patentability).
  - ☐ Results were not useful in determining patentability or understanding the invention.

Comments:

=> file reg
FILE 'REGISTRY' ENTERED AT 11:31:36 ON 20 JAN 2006

Property values tagged with IC are from the ZIC/VINITI data file provided by InfoChem.

STRUCTURE FILE UPDATES: 18 JAN 2006 HIGHEST RN 872163-75-2
DICTIONARY FILE UPDATES: 18 JAN 2006 HIGHEST RN 872163-75-2

New CAS Information Use Policies, enter HELP USAGETERMS for details.

TSCA INFORMATION NOW CURRENT THROUGH JULY 14, 2005

Please note that search-term pricing does apply when conducting SmartSELECT searches.

****
* *
* The CA roles and document type information have been removed from *
* the IDE default display format and the ED field has been added, *
* effective March 20, 2005. A new display format, IDERL, is now *
* available and contains the CA role and document type information. *
* *
****

Structure search iteration limits have been increased. See HELP SLIMITS for details.

REGISTRY includes numerically searchable data for experimental and predicted properties as well as tags indicating availability of experimental property data in the original document. For information on property searching in REGISTRY, refer to:

http://www.cas.org/ONLINE/UG/regprops.html

=> file hcaplu
FILE 'HCAPLUS' ENTERED AT 11:31:41 ON 20 JAN 2006

FILE COVERS 1907 - 20 Jan 2006 VOL 144 ISS 5
FILE LAST UPDATED: 19 Jan 2006 (20060119/ED)

New CAS Information Use Policies, enter HELP USAGETERMS for details.

This file contains CAS Registry Numbers for easy and accurate substance identification.

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=> d que
L2            10 SEA FILE=REGISTRY ABB=ON  (1066-33-7/BI OR 107-13-1/BI OR
                 107-15-3/BI OR 110-18-9/BI OR 1111-78-0/BI OR 124-38-9/BI OR
                 126-98-7/BI OR 506-87-6/BI OR 7664-41-7/BI OR 7732-18-5/BI)
L4             1 SEA FILE=REGISTRY ABB=ON  126-98-7
L5             3 SEA FILE=REGISTRY ABB=ON  L2 AND AMMONIUM
L6             1 SEA FILE=REGISTRY ABB=ON  L2 AND CARBAM?
L7             2 SEA FILE=REGISTRY ABB=ON  L2 AND DIAMINE
L9          2768 SEA FILE=HCAPLUS ABB=ON  L4
L13        38977 SEA FILE=HCAPLUS ABB=ON  L5 OR L6 OR L7
L15            1 SEA FILE=REGISTRY ABB=ON  107-13-1
L16        28444 SEA FILE=HCAPLUS ABB=ON  L15
L17          122 SEA FILE=HCAPLUS ABB=ON  (L16 OR L9)(L)PUR/RL
L18           76 SEA FILE=HCAPLUS ABB=ON  L17 AND (H2O OR AQUEOUS? OR WATER?)
L19           40 SEA FILE=HCAPLUS ABB=ON  L18 AND COLUMN?
L20            1 SEA FILE=HCAPLUS ABB=ON  L19 AND L13
L21            2 SEA FILE=HCAPLUS ABB=ON  L19 AND ALKALIN?
L22          283 SEA FILE=HCAPLUS ABB=ON  (L16 OR L9) AND EXTRACT? AND DISTILL?

L23          238 SEA FILE=HCAPLUS ABB=ON  L22 AND (H2O OR AQUEOUS? OR WATER?)
L24           47 SEA FILE=HCAPLUS ABB=ON  L23 AND ALKALI?
L25            4 SEA FILE=HCAPLUS ABB=ON  L23 AND L13
L26            7 SEA FILE=HCAPLUS ABB=ON  L24 AND GAS?
L27            4 SEA FILE=HCAPLUS ABB=ON  L24 AND VAPOR?
L28         4174 SEA FILE=HCAPLUS ABB=ON  (L16 OR L9)(L)PREP/RL
L29           58 SEA FILE=HCAPLUS ABB=ON  L22 AND L28
L30           47 SEA FILE=HCAPLUS ABB=ON  L23 AND L29
L31            3 SEA FILE=HCAPLUS ABB=ON  L30 AND DECANT?
L32            1 SEA FILE=HCAPLUS ABB=ON  L30 AND L13
L33            8 SEA FILE=HCAPLUS ABB=ON  L30 AND (ALKALINE OR ALKALI OR BASE#
                 OR AMINE#)
L34           21 SEA FILE=HCAPLUS ABB=ON  L20 OR L21 OR (L25 OR L26 OR L27) OR
                 L31 OR L32 OR L33
L35           25 SEA FILE=HCAPLUS ABB=ON  L30 AND (GAS? OR VAPOR?)
L36           40 SEA FILE=HCAPLUS ABB=ON  L34 OR L35

=> d l36 bib abs ind hitstr 1-40

L36  ANSWER 1 OF 40  HCAPLUS  COPYRIGHT 2006 ACS on STN
AN   2005:904397  HCAPLUS
DN   143:230362
TI   Process for the purification of an ammoxidation-derived olefinically
     unsaturated nitrilesusing absorption and extractive
     distillation
IN   Godbole, Sanjay P.; Kantak, Milind V.; Wahnschafft, Oliver M.
PA   USA
SO   U.S. Pat. Appl. Publ., 8 pp.
     CODEN: USXXCO
DT   Patent
LA   English
FAN.CNT 2
     PATENT NO.          KIND   DATE        APPLICATION NO.        DATE
     --------------      ----   --------    --------------------   --------
PI   US 2005187401        A1    20050825    US 2005-31277          20050106
PRAI US 2004-535414P      P     20040109
AB   A process for the recovery and purification of olefinically unsatd. nitriles
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(e.g., acrylonitrile) from a process stream produced by the ammoxidn. of a hydrocarbon feedstock comprises: contacting the process stream comprising the unsatd. nitrile with an **aqueous** quench liquid in a quench apparatus to produce a **gaseous** quench effluent comprising the unsatd. nitrile; contacting the **gaseous** quench effluent with a liquid comprising **water** in an absorber apparatus to form an **aqueous** mixture comprising the absorbed unsatd. nitrile; withdrawing from the absorber apparatus a side-draw stream comprising **water** and a bottoms stream comprising the unsatd. nitrile; introducing the bottoms stream to a first **distillation** column where the bottoms stream is **distilled** in an **extractive distillation** to form a top fraction comprising the unsatd. nitrile, and directing the side-draw stream comprising **water** to the upper portion of the first **distn** . column to assist with the **extractive distillation** of the unsatd. nitrile in the first **distillation** column. A process flow diagram is presented.

IC ICM C07C253-34
INCL 558463000
CC 35-2 (Chemistry of Synthetic High Polymers)
Section cross-reference(s): 23, 48
ST unsatd nitrile purifn absorption **distn**; acrylonitrile purifn absorption **distn**
IT Columns and Towers
(absorption; in a process for the purification of an ammoxidn.-derived olefinically unsatd. nitrilesusing absorption and **extractive distillation**)
IT Monomers
RL: EPR (Engineering process); IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); PREP (Preparation); PROC (Process)
(acrylic; process for the purification of an ammoxidn.-derived olefinically unsatd. nitrilesusing absorption and **extractive distn** .)
IT **Distillation** columns
(**extractive**; in a process for the purification of an ammoxidn.-derived olefinically unsatd. nitrilesusing absorption and **extractive distillation**)
IT **Distillation**
(**extractive**; process for the purification of an ammoxidn.-derived olefinically unsatd. nitrilesusing absorption and **extractive distillation**)
IT Cooling
(of an absorber in a process for the purification of an ammoxidn.-derived olefinically unsatd. nitrilesusing absorption and **extractive distillation**)
IT Absorption
Ammoxidation
(process for the purification of an ammoxidn.-derived olefinically unsatd. nitrilesusing absorption and **extractive distillation**)
IT Nitriles, preparation
RL: EPR (Engineering process); IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); PREP (Preparation); PROC (Process)
(unsatd.; process for the purification of an ammoxidn.-derived olefinically unsatd. nitrilesusing absorption and **extractive distn** .)
IT Coolants
(**water**; for cooling of an absorber in a process for the purification of an ammoxidn.-derived olefinically unsatd. nitrilesusing absorption and **extractive distillation**)

IT 7732-18-5, **Water**, uses
RL: EPR (Engineering process); NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PYP (Physical process); PROC (Process); USES (Uses)
(in a process for the purification of an ammoxidn.-derived olefinically unsatd. nitrilesusing absorption and **extractive distn**.)

IT 75-05-8, Acetonitrile, processes
RL: EPR (Engineering process); PEP (Physical, engineering or chemical process); REM (Removal or disposal); PROC (Process)
(in a process for the purification of an ammoxidn.-derived olefinically unsatd. nitrilesusing absorption and **extractive distn**.)

IT **107-13-1P**, Acrylonitrile, preparation
RL: EPR (Engineering process); IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); **PREP (Preparation)**; PROC (Process)
(process for the purification of an ammoxidn.-derived olefinically unsatd. nitrilesusing absorption and **extractive distillation**)

IT 115-07-1, Propene, reactions 7664-41-7, Ammonia, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(process for the purification of an ammoxidn.-derived olefinically unsatd. nitrilesusing absorption and **extractive distillation**)

IT 7782-44-7, Oxygen, reactions
RL: RGT (Reagent); RACT (Reactant or reagent)
(process for the purification of an ammoxidn.-derived olefinically unsatd. nitrilesusing absorption and **extractive distillation**)

IT **107-13-1P**, Acrylonitrile, preparation
RL: EPR (Engineering process); IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); **PREP (Preparation)**; PROC (Process)
(process for the purification of an ammoxidn.-derived olefinically unsatd. nitrilesusing absorption and **extractive distillation**)

RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)

L36 ANSWER 2 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 2005:696871 HCAPLUS
DN 143:173547
TI Process for the purification of olefinically unsaturated nitriles
IN Godbole, Sanjay P.; Kantak, Milind V.; Wahnschafft, Oliver M.
PA The Standard Oil Company, USA
SO PCT Int. Appl., 19 pp.
CODEN: PIXXD2
DT Patent
LA English
FAN.CNT 2

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	WO 2005070880	A1	20050804	WO 2005-US557	20050106

W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,

LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI,
NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY,
TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM,
AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK,
EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT,
RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML,
MR, NE, SN, TD, TG

PRAI US 2004-535414P P 20040109

AB A process for the recovery and purification of olefinically unsatd. nitriles (e.g., acrylonitrile) from a process stream comprises: (a) contacting a process stream comprising an olefinically unsatd. nitrile with an **aqueous** quench liquid in a quench apparatus to produce a **gaseous** quench effluent comprising the olefinically unsatd. nitrile; (b) contacting the **gaseous** quench effluent with a liquid comprising **water** in an absorber apparatus to form an **aqueous** mixture comprising absorbed olefinically unsatd. nitrile; (c) withdrawing from the absorber apparatus a side-draw stream comprising **water** and a stream comprising an olefinically unsatd. nitrile; (d) introducing the stream comprising the olefinically unsatd. nitrile into a first **distillation** column where the stream is **distilled** in an **extractive distillation** to form a fraction comprising an olefinically unsatd. nitrile; and (e) directing the side-draw stream comprising **water** to the first **distillation** column for the **extractive distillation** of the olefinically unsatd. nitrile in the first **distillation** column. A process flow diagram is presented.

IC ICM C07C253-34
ICS C07C255-08

CC 35-2 (Chemistry of Synthetic High Polymers)
Section cross-reference(s): 23, 48

ST olefinically unsatd nitrile **distn** purifn; acrylonitrile **distn** purifn

IT Alkenes, reactions
RL: EPR (Engineering process); PEP (Physical, engineering or chemical process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent)
(ammoxidn. of)

IT **Distillation**
(**extractive**; in a process for the purification of olefinically unsatd. nitriles)

IT Ammoxidation
Distillation columns
(in a process for the purification of olefinically unsatd. nitriles)

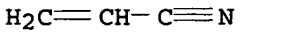
IT Nitriles, preparation
RL: EPR (Engineering process); PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); PREP (Preparation); PROC (Process)
(unsatd.; process for the purification of olefinically unsatd. nitriles)

IT 115-07-1, Propene, reactions
RL: EPR (Engineering process); PEP (Physical, engineering or chemical process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent)
(ammoxidn. of)

IT 7732-18-5, **Water**, uses
RL: EPR (Engineering process); NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)
(in a process for the purification of olefinically unsatd. nitriles)

IT **107-13-1P**, Acrylonitrile, preparation
RL: EPR (Engineering process); PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); **PREP (Preparation)**; PROC (Process)
(process for the purification of olefinically unsatd. nitriles)

IT **107-13-1P**, Acrylonitrile, preparation
RL: EPR (Engineering process); PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); **PREP (Preparation)**; PROC (Process)
(process for the purification of olefinically unsatd. nitriles)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)



RE.CNT 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L36 ANSWER 3 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 2004:606433 HCAPLUS
DN 141:140908
TI **Extractive distillation** process for recovering acrylonitrile or methacrylonitrile from ammoxidation reaction effluents
IN Godbole, Sanjay P.; Cesa, Mark C.
PA The Standard Oil Company, USA
SO PCT Int. Appl., 12 pp.
CODEN: PIXXD2
DT Patent
LA English
FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI WO 2004063145	A1	20040729	WO 2003-US38691	20031205
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
CA 2516401	AA	20040729	CA 2003-2516401	20031205
EP 1590320	A1	20051102	EP 2003-796689	20031205
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, HU, SK				
US 2004181086	A1	20040916	US 2003-736387	20031215
PRAI US 2003-437836P	P	20030103		
WO 2003-US38691	W	20031205		

AB A process for the recovery of acrylonitrile or methacrylonitrile from an **aqueous** solution comprises subjecting the solution to a **water extractive distillation** by feeding the solution to a **distillation column** and performing the **extractive distillation** and using solvent **water** introduced at the top of the **column**, removing a first overhead **vapor** stream of acrylonitrile or methacrylonitrile with some **water** from the top of the **column**, and a first liquid stream containing **water** and impurities from the bottom of the **column**, the contents of the **column** maintained at a substantially neutral pH by adding a sufficient amount of at least one **alkaline** compound selected from ammonium carbonate, ammonium bicarbonate, ammonium carbamate, and alkylene diamines (e.g., TMEDA) to the overhead **decanter** and/or to the

solvent **water.**

IC ICM C07C253-26
ICS C07C253-34; C07C255-08

CC 35-2 (Chemistry of Synthetic High Polymers)
Section cross-reference(s): 23, 48

ST acrylonitrile monomer recovery **extractive distn;**
methacrylonitrile monomer recovery **extractive distn**

IT Monomers
RL: PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); PREP (Preparation); PROC (Process)
(acrylonitrile or methacrylonitrile; **extractive distn**
. process for recovering acrylonitrile or methacrylonitrile from ammoxidn. reaction effluents)

IT Separators
(**decanters**; in an **extractive distillation**
process for recovering acrylonitrile or methacrylonitrile from ammoxidn. reaction effluents)

IT **Amines**, reactions
RL: RGT (Reagent); RACT (Reactant or reagent)
(diamines, aliphatic, **bases**; in an **extractive distillation** process for recovering acrylonitrile or methacrylonitrile from ammoxidn. reaction effluents)

IT **Distillation**
Distillation columns
(**extractive**; **extractive distillation** process for recovering acrylonitrile or methacrylonitrile from ammoxidn. reaction effluents)

IT **Bases**, reactions
RL: RGT (Reagent); RACT (Reactant or reagent)
(in an **extractive distillation** process for recovering acrylonitrile or methacrylonitrile from ammoxidn. reaction effluents)

IT **506-87-6P**, Ammonium carbonate
RL: PNU (Preparation, unclassified); RGT (Reagent); PREP (Preparation); RACT (Reactant or reagent)
(**base**; in an **extractive distillation** process for recovering acrylonitrile or methacrylonitrile from ammoxidn. reaction effluents)

IT **107-15-3**, Ethylene diamine, reactions **110-18-9**, TMEDA **1066-33-7**, Ammonium bicarbonate **1111-78-0**, Ammonium carbamate
RL: RGT (Reagent); RACT (Reactant or reagent)
(**base**; in an **extractive distillation** process for recovering acrylonitrile or methacrylonitrile from ammoxidn. reaction effluents)

IT **107-13-1P**, Acrylonitrile, preparation **126-98-7P**, Methacrylonitrile
RL: PEP (Physical, engineering or chemical process); **PUR (Purification or recovery)**; PYP (Physical process); **PREP (Preparation)**; PROC (Process)
(**extractive distillation** process for recovering acrylonitrile or methacrylonitrile from ammoxidn. reaction effluents)

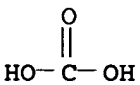
IT 124-38-9, Carbon dioxide, reactions 7664-41-7, Ammonia, reactions
RL: RGT (Reagent); RACT (Reactant or reagent)
(in the in-situ preparation of ammonium carbonate)

IT 7732-18-5, **Water**, reactions
RL: NUU (Other use, unclassified); RGT (Reagent); RACT (Reactant or reagent); USES (Uses)
(solvent; **extractive distillation** process for recovering acrylonitrile or methacrylonitrile from ammoxidn. reaction effluents)

IT **506-87-6P**, Ammonium carbonate

RL: PNU (Preparation, unclassified); RGT (Reagent); PREP (Preparation); RACT (Reactant or reagent)
(**base**; in an **extractive distillation** process for recovering acrylonitrile or methacrylonitrile from ammoxidn. reaction effluents)

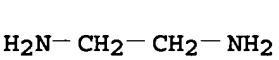
RN 506-87-6 HCAPLUS
CN Carbonic acid, diammonium salt (8CI, 9CI) (CA INDEX NAME)



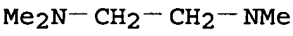
●2 NH_3

IT **107-15-3**, Ethylene diamine, reactions **110-18-9**, TMEDA **1066-33-7**, Ammonium bicarbonate **1111-78-0**, Ammonium carbamate
RL: RGT (Reagent); RACT (Reactant or reagent)
(**base**; in an **extractive distillation** process for recovering acrylonitrile or methacrylonitrile from ammoxidn. reaction effluents)

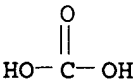
RN 107-15-3 HCAPLUS
CN 1,2-Ethanediamine (9CI) (CA INDEX NAME)



RN 110-18-9 HCAPLUS
CN 1,2-Ethanediamine, N,N,N',N'-tetramethyl- (9CI) (CA INDEX NAME)

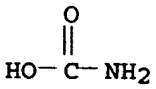


RN 1066-33-7 HCAPLUS
CN Carbonic acid, monoammonium salt (8CI, 9CI) (CA INDEX NAME)



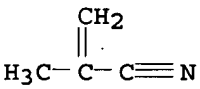
● NH_3

RN 1111-78-0 HCAPLUS
CN Carbamic acid, monoammonium salt (8CI, 9CI) (CA INDEX NAME)



IT **107-13-1P**, Acrylonitrile, preparation **126-98-7P**, Methacrylonitrile
RL: PEP (Physical, engineering or chemical process); **PUR (Purification or recovery)**; PYP (Physical process); **PREP (Preparation)**; PROC (Process)
(extractive distillation process for recovering acrylonitrile or methacrylonitrile from ammoxidn. reaction effluents)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)

RN 126-98-7 HCAPLUS
CN 2-Propenenitrile, 2-methyl- (9CI) (CA INDEX NAME)



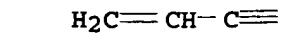
L36 ANSWER 4 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 2004:473397 HCAPLUS
DN 141:24127
TI Method for inhibiting polymerization during the recovery and purification of unsaturated mononitriles
IN Rosen, Bruce I.; Firth, Bruce E.
PA USA
SO U.S. Pat. Appl. Publ., 12 pp.
CODEN: USXXCO
DT Patent
LA English
FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI US 2004110977	A1	20040610	US 2002-309962	20021204
US 6984749	B2	20060110		
CA 2506409	AA	20040624	CA 2003-2506409	20031112
WO 2004052842	A1	20040624	WO 2003-US36060	20031112

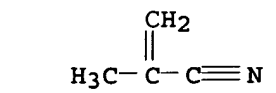
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW
RW: BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ,

BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK,
TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG
EP 1567481 A1 20050831 EP 2003-781907 20031112
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT,
IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, HU, SK
BR 2003016857 A 20051018 BR 2003-16857 20031112
US 2004249182 A1 20041209 US 2004-852277 20040524
PRAI US 2002-309962 A 20021204
WO 2003-US36060 W 20031112
OS MARPAT 141:24127
AB Economical processes for recovery and refining of valuable N-containing organic compds. formed by catalytic oxidation of ≥1 feed compound selected from propane, propylene, isobutane and isobutylene in the presence of NH3 to produce a **gaseous** effluent containing unsatd. mononitriles are described. Processes include quenching the **gaseous** reactor effluent with an **aqueous** quench liquid; forming an **aqueous** solution comprising the corresponding unsatd. mononitrile, HCN and other organic coproducts; and using an integrated sequence of distns. and phase sepns. to recover for recycle of a useful **aqueous** liquid, and obtain the desired N-containing products. **Aqueous** solns. are fractionated in an integrated system of multi-stage columns while introducing an effective polymerization inhibiting amount of ≥1 member of a preselected class of p-phenylenediamine compds. such as N,N'-di-sec-butyl-p-phenylenediamine.
IC ICM C07C253-26
INCL 558320000
CC 35-2 (Chemistry of Synthetic High Polymers)
Section cross-reference(s): 23
ST acrylonitrile recovery polymn inhibiting phenylenediamine
IT **Distillation**
Extraction
Phase separation
Polymerization inhibitors
(phenylenediamine compds. for inhibiting polymerization during the recovery and purification of unsatd. mononitriles)
IT 101-96-2, N,N'-Di-sec-butyl-p-phenylenediamine 4251-01-8, N,N'-Di-sec-propyl-p-phenylenediamine 10368-05-5, N,N'-Diisobutyl-p-phenylenediamine 42574-83-4
RL: CAT (Catalyst use); USES (Uses)
(phenylenediamine compds. for inhibiting polymerization during the recovery and purification of unsatd. mononitriles)
IT **107-13-1P**, Acrylonitrile, preparation **126-98-7P**, Methacrylonitrile
RL: PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); **PREP (Preparation)**; PROC (Process)
(phenylenediamine compds. for inhibiting polymerization during the recovery and purification of unsatd. mononitriles)
IT 115-07-1, Propylene, reactions 115-11-7, Isobutylene, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(phenylenediamine compds. for inhibiting polymerization during the recovery and purification of unsatd. mononitriles)
IT **107-13-1P**, Acrylonitrile, preparation **126-98-7P**, Methacrylonitrile
RL: PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); **PREP (Preparation)**; PROC (Process)
(phenylenediamine compds. for inhibiting polymerization during the recovery and purification of unsatd. mononitriles)
RN 107-13-1 HCAPLUS

CN 2-Propenenitrile (9CI) (CA INDEX NAME)



RN 126-98-7 HCAPLUS
CN 2-Propenenitrile, 2-methyl- (9CI) (CA INDEX NAME)



RE.CNT 18 THERE ARE 18 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

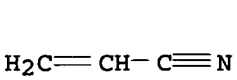
L36 ANSWER 5 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 2000:337482 HCAPLUS
DN 132:308815
TI Recovery and refining of olefinic nitrile
IN Guan, Xingya; Zhang, Hui; Fang, Yongcheng
PA Sino Petro-Chemical Corp., Peop. Rep. China
SO Faming Zhuanli Shenqing Gongkai Shuomingshu, 12 pp.
CODEN: CNXXEV
DT Patent
LA Chinese
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	CN 1217324	A	19990526	CN 1997-106712	19971113
	CN 1059897	B	20001227		
PRAI	CN 1997-106712		19971113		

AB The process comprises feeding the crude olefinic nitrile **gas** to the bottom of quenching tower, cooling successively with a **water**-containing cooling liquid and at pH <7 with the temperature controlled at 70-90° for the lower section, 75-85° for the medium section and 25-45° for the upper section, feeding the condensed liquid to **extraction** tower, feeding the olefinic nitrile and HCN containing un-condensed liquid to absorption tower, **distilling** to remove **water** and impurity, **distilling** the condensed solution in the presence of acetic acid as stabilizer in HCN **distillation** tower with the pressure at the top of tower controlled at -0.05 to 0 MPa to obtain olefinic nitrile liquid and HCN **gas**; and separating the liquid from the side of the tower to obtain organic phase and solution for recycle. The process is preferably used for preparing acrylonitrile. Acrylonitrile is synthesized by ammoxidn. of propene with NH3 and air at 440° and 0.5 kg/cm2. Acrylic acid, cyanic acid and acetonitrile are the byproducts of acrylonitrile synthesis.

IC ICM C07C255-08
ICS C07C253-34
CC 35-2 (Chemistry of Synthetic High Polymers)
ST olefinic nitrile recovery refining acrylonitrile synthesis
IT Ammoxidation
(recovery and refining of olefinic nitrile)
IT Nitriles, preparation
RL: IMF (Industrial manufacture); PREP (Preparation)
(unsatd.; recovery and refining of olefinic nitrile)
IT **107-13-1P**, Acrylonitrile, preparation

RL: IMF (Industrial manufacture); **PREP (Preparation)**
(recovery and refining of olefinic nitrile)
IT 115-07-1, Propene, reactions 7664-41-7, Ammonia, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(recovery and refining of olefinic nitrile)
IT 64-19-7, Acetic acid, uses
RL: NUU (Other use, unclassified); USES (Uses)
(stabilizer; recovery and refining of olefinic nitrile)
IT **107-13-1P**, Acrylonitrile, preparation
RL: IMF (Industrial manufacture); **PREP (Preparation)**
(recovery and refining of olefinic nitrile)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)



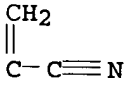
L36 ANSWER 6 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1999:622330 HCAPLUS
DN 131:229159
TI Recovery of organic compounds from the process flare headers of ammoxidation processes
IN Keckler, Kenneth P.; Godbole, Sanjay P.
PA The Standard Oil Company, USA
SO U.S., 4 pp.
CODEN: USXXAM
DT Patent
LA English
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 5959134	A	19990928	US 1998-82403	19980520
	CA 2332502	AA	19991125	CA 1999-2332502	19990518
	WO 9959963	A1	19991125	WO 1999-US11030	19990518
	W: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM				
	RW: GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG				
	AU 9940866	A1	19991206	AU 1999-40866	19990518
	BR 9910601	A	20010116	BR 1999-10601	19990518
	TR 200003412	T2	20010321	TR 2000-200003412	19990518
	EP 1087936	A1	20010404	EP 1999-924343	19990518
	R: AT, BE, DE, ES, FR, GB, NL				
	JP 2002515479	T2	20020528	JP 2000-549582	19990518
	RU 2258695	C2	20050820	RU 2000-131596	19990518
	TW 584575	B	20040421	TW 1999-88108210	19990608
	BG 104923	A	20010531	BG 2000-104923	20001107
PRAI	US 1998-82403	A	19980520		
	WO 1999-US11030	W	19990518		

AB A process for the enhanced recovery of waste orgs. (e.g., hydrogen cyanide) from the process flare material obtained from the reactor effluent of an ammoxidn. reaction of propylene or isobutylene is described which comprises directing a portion of the process flare header material to an organic recovery process selected from **aqueous**-phase

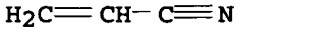
countercurrent scrubbing, organic-phase countercurrent scrubbing, **aq**
.-phase co-current scrubbing, organic-phase co-current scrubbing,
distillation, **extraction**, leaching, adsorption, absorption,
selective condensation, and selective reaction.

IC ICM C07C253-00
INCL 558320000
CC 35-2 (Chemistry of Synthetic High Polymers)
Section cross-reference(s): 23, 45, 48, 59
ST hydrogen cyanide recovery ammoxidn process; org compd recovery ammoxidn process waste **gas** scrubbing
IT Ammoxidation
(recovery of organic compds. from the process flare headers of ammoxidn. processes)
IT Absorption
Adsorption
Distillation
Extraction
Scrubbing
(recovery of organic compds. from the process flare headers of ammoxidn. processes via)
IT **Distillation** columns
(recovery of organic compds. from the process flare headers of ammoxidn. processes via a contactor in)
IT **126-98-7P**, Methacrylonitrile
RL: IMF (Industrial manufacture); **PREP (Preparation)**
(recovery of organic compds. from the process flare headers of ammoxidn. processes)
IT **107-13-1P**, Acrylonitrile, preparation
RL: IMF (Industrial manufacture); PUR (Purification or recovery); **PREP (Preparation)**
(recovery of organic compds. from the process flare headers of ammoxidn. processes)
IT 74-90-8P, Prussic acid, preparation
RL: PUR (Purification or recovery); PREP (Preparation)
(recovery of organic compds. from the process flare headers of ammoxidn. processes)
IT 115-07-1, Propene, reactions 115-11-7, Isobutene, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(recovery of organic compds. from the process flare headers of ammoxidn. processes)
IT 7732-18-5, **Water**, uses
RL: NUU (Other use, unclassified); USES (Uses)
(solvent; recovery of organic compds. from the process flare headers of ammoxidn. processes)
IT **126-98-7P**, Methacrylonitrile
RL: IMF (Industrial manufacture); **PREP (Preparation)**
(recovery of organic compds. from the process flare headers of ammoxidn. processes)
RN 126-98-7 HCAPLUS
CN 2-Propenenitrile, 2-methyl- (9CI) (CA INDEX NAME)



IT **107-13-1P**, Acrylonitrile, preparation
RL: IMF (Industrial manufacture); PUR (Purification or recovery); **PREP (Preparation)**

(recovery of organic compds. from the process flare headers of ammoxidn. processes)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)



RE.CNT 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

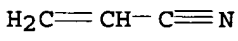
L36 ANSWER 7 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1998:787995 HCAPLUS
DN 130:54119
TI **Extractive distillation**: Separating close-boiling-point components
AU Lee, Fu-Ming
CS GTC Technology Corp., Houston, TX, 77077, USA
SO Chemical Engineering (New York) (1998), 105(12), 112-116, 118, 120-121
CODEN: CHEEA3; ISSN: 0009-2460
PB McGraw-Hill Companies, Inc.
DT Journal
LA English
AB **Extractive distillation** has been used in the chemical process industries for years, although not as widely as traditional **distn**. and azeotropic **distillation** The selection of cosolvents using polarity (e.g., dielec. constant) as an initial guideline is discussed for various hydrocarbon sepns. using **extractive distillation**
CC 48-1 (Unit Operations and Processes)
Section cross-reference(s): 51
ST **extractive distn** close boiling point component
IT Solvents
(cosolvents; **extractive distillation** for separation of close b.p. components)
IT Dielectric constant
Polarity
(**extractive distillation** for separation of close b.p. components)
IT Hydrocarbons, processes
Natural gas condensates
RL: PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PREP (Preparation); PROC (Process)
(**extractive distillation** for separation of close b.p. components)
IT **Distillation**
(**extractive**; **extractive distillation** for separation of close b.p. components)
IT Solvents
(mixts.; MIST; **extractive distillation** for separation of close b.p. components)
IT Volatility
(relative; **extractive distillation** for separation of close b.p. components)
IT 108-08-7P, 2,4-Dimethylpentane 108-88-3P, Toluene, processes 110-82-7P, Cyclohexane, processes 142-82-5P, n-Heptane, processes 464-06-2P, 2,2,3-Trimethylbutane 562-49-2P, 3,3-Dimethylpentane 565-59-3P, 2,3-Dimethylpentane 589-34-4P, 3-Methylhexane 590-35-2P, 2,2-Dimethylpentane 591-76-4P, 2-Methylhexane 28729-52-4P, Dimethylcyclopentane

RL: PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PREP (Preparation); PROC (Process)
(**extractive distillation** for separation of close b.p. components)

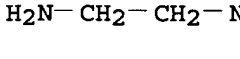
IT 56-81-5, Glycerol, properties 57-55-6, 1,2-Propanediol, properties 62-53-3, Aniline, properties 64-17-5, Ethanol, properties 67-56-1, Methanol, properties 67-71-0, Dimethylsulfone 71-23-8, 1-Propanol, properties 71-36-3, 1-Butanol, properties 75-05-8, Acetonitrile, properties 75-12-7, Formamide, properties 75-50-3, Trimethylamine, properties 75-52-5, Nitromethane, properties 78-81-9, Iso-Butylamine 78-83-1, 2-Methyl-1-propanol, properties 78-92-2, 2-Butanol 87-99-0, Xylitol 95-48-7, o-Cresol, properties 95-65-8, 3,4-Dimethylphenol 96-41-3, Cyclopentanol 96-49-1, Ethylene carbonate 100-41-4, Ethylbenzene, properties 100-47-0, Benzonitrile, properties 103-69-5, n-Ethylaniline 107-12-0, Propionitrile **107-13-1**, Acrylonitrile, properties **107-15-3**, Ethylene diamine, properties 107-21-1, Ethylene glycol, properties 107-87-9, 2-Pentanone 108-39-4, properties 108-93-0, Cyclohexanol, properties 108-95-2, Phenol, properties 109-06-8, 2-Methyl pyridine 109-86-4, 2-Methoxyethanol 109-99-9, Tetrahydrofuran, properties 110-59-8, Pentanenitrile 110-63-4, 1,4-Butanediol, properties 110-80-5, 2-Ethoxyethanol 110-91-8, Morpholine, properties 110-96-3, Diisobutylamine 111-13-7, 2-Octanone 111-27-3, 1-Hexanol, properties 111-70-6, 1-Heptanol 111-87-5, 1-Octanol, properties 111-92-2, Dibutylamine 112-27-6, Triethylene glycol 112-30-1, 1-Decanol 112-53-8, 1-Dodecanol 112-72-1, 1-Tetradecanol 121-69-7, N,N-Dimethylaniline, properties 123-39-7, N-Methylformamide 123-91-1, 1,4-Dioxane, properties 123-96-6, 2-Octanol 124-40-3, Dimethylamine, properties 126-33-0, Sulfolane 127-19-5, N,N-Dimethylacetamide 137-32-6, 2-Methyl-1-butanol 142-68-7, Tetrahydropyran 504-63-2, 1,3-Propanediol 543-49-7, 2-Heptanol 589-55-9, 4-Heptanol 589-82-2, 3-Heptanol 591-78-6, 2-Hexanone 598-03-8, Di-n-propyl sulfone 680-31-9, Tris(dimethylamino)phosphine oxide, properties 872-50-4, N-Methyl pyrrolidone, properties 872-93-5, 3-Methylsulfolane 6032-29-7, 2-Pentanol 7443-70-1, cis-2-Methylcyclohexanol 7732-18-5, **Water**, properties 18720-62-2, 2-Methyl-3-heptanol
RL: PRP (Properties)
(**extractive distillation** for separation of close b.p. components)

IT **107-13-1**, Acrylonitrile, properties **107-15-3**, Ethylene diamine, properties
RL: PRP (Properties)
(**extractive distillation** for separation of close b.p. components)

RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)



RN 107-15-3 HCAPLUS
CN 1,2-Ethanediamine (9CI) (CA INDEX NAME)



RE.CNT 15 THERE ARE 15 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

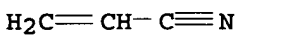
L36 ANSWER 8 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1989:58282 HCAPLUS
DN 110:58282
TI Process for recovery of acrylonitrile and lactonitrile from acrylonitrile synthesis mixture residues by **extraction** with salt solutions
IN Schnurpfeil, Dieter; Parthey, Manfred; Wiegner, Jens Peter
PA VEB Chemische Werk, Ger. Dem. Rep.
SO Ger. (East), 3 pp.
CODEN: GEXXA8
DT Patent
LA German
FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI DD 257066	A1	19880601	DD 1987-299256	19870115
PRAI DD 1987-299256		19870115		

AB Lactonitrile and acrylonitrile are recovered from nitrile-containing organic solns. (containing 35-55% lactonitrile and 15-25% acrylonitrile) obtained from **distillation** residues prepared during acrylonitrile synthesis from C2H2 and HCN, by **extraction** with **aqueous** salts solns. and subsequent back **extraction** Solns. containing 20-30% **alkali** metal halides and/or **alkaline** earth metal halides are used with an **extraction** solution-**distillation** residue ratio of 2-5:1. This process facilitates waste stream processing and overcomes potential ecol. problems. Thus, a **distillation** residue (100 mL), containing acetaldehyde 8, acrylonitrile 15, cyanobutadiene 3, chlorocyclobutadiene 11, lactonitrile 48, and **water** 15, was **extracted** with 200 mL of 25% **aqueous** BaCl2 solution, producing an organic phase containing chlorocyanobutenes 75, cyanobutadienes 15, lactonitrile 6, acrylonitrile 4, and **water** 2%. This **aqueous** phase was back **extracted** 3 times with 100-mL portions of CH2Cl2, and the solvent evaporated, producing an **extract** consisting of lactonitrile 70, acrylonitrile 20, and **water** 10%.

IC ICM C07C121-34
ICS C07C121-32; C07C120-02
CC 35-2 (Chemistry of Synthetic High Polymers)
Section cross-reference(s): 23
ST lactonitrile acrylonitrile **distn** residue recovery; barium chloride **extn** lactonitrile recovery; **alk** earth halide **extn** acrylonitrile; **alkali** metal halide **extn** acrylonitrile
IT **Alkali** metal halides, uses and miscellaneous
Alkaline earth halides
RL: USES (Uses)
(solns., **extraction** of acrylonitrile and lactonitrile by, from acrylonitrile-synthesis **distillation** residues)
IT **107-13-1P**, Acrylonitrile, preparation
RL: **PREP (Preparation)**
(**extraction** of lactonitrile and, from acrylonitrile-manufacture **distillation** residues, with **alkaline** earth-and/or **alkali** metal halide solns.)
IT 78-97-7P, Lactonitrile
RL: PREP (Preparation)
(recovery of acrylonitrile and, from acrylonitrile-manufacture **distn**. residues, by **extraction** with **alkaline** earth-and/or **alkali** metal halides)
IT 7647-14-5, Sodium chloride, uses and miscellaneous 10361-37-2, Barium chloride, uses and miscellaneous
RL: USES (Uses)
(solns., **extraction** of acrylonitrile and lactonitrile with, from

acrylonitrile-synthesis **distillation** residues)
IT **107-13-1P**, Acrylonitrile, preparation
RL: **PREP (Preparation)**
(**extraction** of lactonitrile and, from acrylonitrile-manufacture **distillation** residues, with **alkaline** earth-and/or **alkali** metal halide solns.)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)

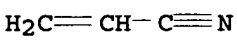


L36 ANSWER 9 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1988:551906 HCAPLUS
DN 109:151906
TI Simultaneous removal of products and byproducts from **gases** from the ammoxidation of hydrocarbons
IN Schymalla, Alfred; Martin, Andreas; French, Juergen; Mueller, Guenter; Luecke, Bernhard; Seeboth, Helmuth; Herbig, Herbert; Krause, Bernd
PA Akademie der Wissenschaften der DDR, Ger. Dem. Rep.
SO Ger. (East), 5 pp.
CODEN: GEXXA8
DT Patent
LA German
FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI DD 251876	A3	19871202	DD 1982-239747	19820511
PRAI DD 1982-239747		19820511		

OS CASREACT 109:151906
AB Nitriles prepared by ammoxidn. of alkyl-substituted hydrocarbons (e.g., acrylonitrile and 4-methoxybenzonitrile) are separated from the reaction **gases** by scrubbing with an emulsion of mutually immiscible solvents (e.g., PhMe and **aqueous** NaOH, or PhMe and **H2O**). In the continuous countercurrent scrubbing process, the emulsion breaks once it leaves the turbulent mixing environment and allows each product or byproduct to be removed from the solvent by **extraction** or **distillation**
IC ICM B01D053-14
CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)
Section cross-reference(s): 48
ST nitrile manuf ammoxidn hydrocarbon; countercurrent scrubbing ammoxidn reaction mixt
IT Hydrocarbons, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(ammoxidn. of, nitriles from)
IT Nitriles, preparation
RL: PREP (Preparation)
(manufacture of, by hydrocarbon ammoxidn.)
IT Ammoxidation
(of hydrocarbons, nitrile manufacture by)
IT 115-07-1, Propylene, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(ammoxidn. of, acrylonitrile from)
IT 104-93-8, 4-Methoxytoluene
RL: PROC (Process)
(ammoxidn. of, methoxybenzonitrile from)
IT 7664-41-7, Ammonia, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)
(ammoxidn. with, of hydrocarbons, nitriles from)
IT 874-90-8P, 4-Methoxybenzonitrile
RL: PREP (Preparation)
(manufacture of, by ammoxidn. of methoxytoluene)
IT **107-13-1P**, Acrylonitrile, preparation
RL: **PREP (Preparation)**
(manufacture of, by propylene ammoxidn.)
IT 1310-73-2, Sodium hydroxide, uses and miscellaneous
RL: USES (Uses)
(solvents, with toluene, for nitrile removal from ammoxidn. reaction mixts.)
IT 108-88-3, Toluene, uses and miscellaneous
RL: USES (Uses)
(solvents, with **water** or sodium hydroxide, for removal of nitriles from ammoxidn. reaction mixts.)
IT **107-13-1P**, Acrylonitrile, preparation
RL: **PREP (Preparation)**
(manufacture of, by propylene ammoxidn.)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)

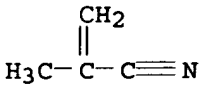


L36 ANSWER 10 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1987:33593 HCAPLUS
DN 106:33593
TI Energy-efficient process for recovery of unsaturated nitriles
IN Katsuta, Kazumasa
PA Asahi Chemical Industry Co., Ltd., Japan
SO Jpn. Kokai Tokkyo Koho, 3 pp.
CODEN: JKXXAF
DT Patent
LA Japanese
FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI JP 61180757	A2	19860813	JP 1985-20597	19850205
PRAI JP 1985-20597		19850205		

AB In the recovery of unsatd. nitriles (e.g., methacrylonitrile) by the **extraction distillation** of the unsatd. nitrile-containing ammoxidn. mixts. absorbed in **water**, the **extraction distillation** mixture was discharged as a side cut which was then phase-separated in a **decanter**, and the oil layer was fed to the recovery tower for removal of HCN and **water** and the **aqueous** layer was recycled to the **extraction distillation** tower.
IC ICM C07C121-32
ICS C07C120-00
CC 35-2 (Chemistry of Synthetic High Polymers)
Section cross-reference(s): 23
ST methacrylonitrile recovery energy efficiency; ammoxidn isobutene methacrylonitrile recovery
IT Ammoxidation
(of isobutene, methacrylonitrile recovery in)
IT Energy
(saving of, in recovery of methacrylonitrile)
IT 115-11-7, Isobutene, reactions

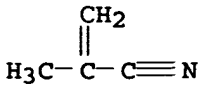
RL: RCT (Reactant); RACT (Reactant or reagent)
(ammoxidn. of, methacrylonitrile recovery in)
IT **126-98-7P**, Methacrylonitrile
RL: **PREP (Preparation)**
(recovery of, from ammoxidn. mixture of isobutene)
IT **126-98-7P**, Methacrylonitrile
RL: **PREP (Preparation)**
(recovery of, from ammoxidn. mixture of isobutene)
RN 126-98-7 HCAPLUS
CN 2-Propenenitrile, 2-methyl- (9CI) (CA INDEX NAME)



L36 ANSWER 11 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1984:511541 HCAPLUS
DN 101:111541
TI Methacrylonitrile recovery
PA Asahi Chemical Industry Co., Ltd., Japan
SO Jpn. Kokai Tokkyo Koho, 3 pp.
CODEN: JKXXAF
DT Patent
LA Japanese
FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI JP 59053454	A2	19840328	JP 1982-164288	19820921
JP 61033810	B4	19860804		
PRAI JP 1982-164288		19820921		

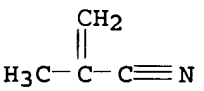
AB Hot propylene ammoxidn. **gas** containing 4.8% methacrylonitrile [**126-98-7**] was cooled from 200° to 36° in a cooling tower by contact with circulating cold **H2O** to give 2 layers at the bottom. The organic layer was separated and bypassed to **extractive distillation**, while the **aqueous** layer was cooled and recycled to the top, thus reducing the load of the absorption step. A higher temperature, e.g. 42°, gave a homogeneous bottom mixture
IC C07C121-32; C07C120-00
CC 35-2 (Chemistry of Synthetic High Polymers)
Section cross-reference(s): 45
ST methacrylonitrile recovery **water** absorption; **distn** methacrylonitrile ammoxidn **gas**
IT **Distillation** apparatus
(for separating methacrylonitrile from propylene ammoxidn. **gas**)
IT **126-98-7P**
RL: **PREP (Preparation)**
(recovery of, from propylene ammoxidn. **gas**, by cold **water** absorption and **extractive distillation**)
IT **126-98-7P**
RL: **PREP (Preparation)**
(recovery of, from propylene ammoxidn. **gas**, by cold **water** absorption and **extractive distillation**)
RN 126-98-7 HCAPLUS
CN 2-Propenenitrile, 2-methyl- (9CI) (CA INDEX NAME)



L36 ANSWER 12 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1984:511540 HCAPLUS
DN 101:111540
TI Methacrylonitrile recovery
PA Asahi Chemical Industry Co., Ltd., Japan
SO Jpn. Kokai Tokkyo Koho, 3 pp.
CODEN: JKXXAF
DT Patent
LA Japanese
FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI JP 59053452	A2	19840328	JP 1982-164286	19820921
JP 61058468	B4	19861211		
PRAI JP 1982-164286		19820921		

AB The methacrylonitrile (I) [**126-98-7**] in propylene ammoxidn. **gas** was absorbed with a min. amount of cold **H2O** to give a 2-layer bottom mixture, e.g. an **aqueous** layer containing 2.9% I and an organic layer containing 87% I. Each layer was sep. fed to a 68-plate column for **extractive distillation**, e.g. at the 42nd and 32nd plate, resp. This improved the energy balance.
IC C07C121-32; C07C120-00
CC 35-2 (Chemistry of Synthetic High Polymers)
Section cross-reference(s): 45
ST ammoxidn **gas** methacrylonitrile recovery; cold **water** absorption methacrylonitrile
IT **126-98-7P**
RL: **PREP (Preparation)**
(recovery of, from propylene ammoxidn. **gas**, by cold **water** absorption)
IT **126-98-7P**
RL: **PREP (Preparation)**
(recovery of, from propylene ammoxidn. **gas**, by cold **water** absorption)
RN 126-98-7 HCAPLUS
CN 2-Propenenitrile, 2-methyl- (9CI) (CA INDEX NAME)



L36 ANSWER 13 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1984:511538 HCAPLUS
DN 101:111538
TI Methacrylonitrile purification
PA Asahi Chemical Industry Co., Ltd., Japan
SO Jpn. Kokai Tokkyo Koho, 4 pp.
CODEN: JKXXAF
DT Patent
LA Japanese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 59053453	A2	19840328	JP 1982-164287	19820921
PRAI	JP 1982-164287		19820921		

AB The bottom fraction of a **distillation** column containing 90% methacrylonitrile (I) [**126-98-7**] and 10% isobutyronitrile (II) [78-82-0] was recycled to a circulating cooling **water** tower for hot ammoxidn. **gas**, and the II contaminant was removed by **extractive distillation** The recycling minimized loss of I.

IC C07C121-32; C07C120-00

CC 35-2 (Chemistry of Synthetic High Polymers)
Section cross-reference(s): 45

ST methacrylonitrile purifn **distn**; isobutyronitrile removal methacrylonitrile **distn**

IT **Distillation** apparatus
(for removal of isobutyronitrile from methacrylonitrile)

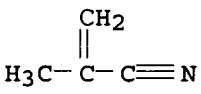
IT **126-98-7P**
RL: PUR (Purification or recovery); **PREP (Preparation)**
(purification of, by **extractive distillation**, for removal of isobutyronitrile)

IT 78-82-0
RL: REM (Removal or disposal); PROC (Process)
(removal of, from methacrylonitrile, by **extractive distillation**)

IT **126-98-7P**
RL: PUR (Purification or recovery); **PREP (Preparation)**
(purification of, by **extractive distillation**, for removal of isobutyronitrile)

RN 126-98-7 HCAPLUS

CN 2-Propenenitrile, 2-methyl- (9CI) (CA INDEX NAME)



L36 ANSWER 14 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1983:423085 HCAPLUS

DN 99:23085

TI Recovery and purification of olefinic nitriles

IN Wu, Hsin C.

PA Standard Oil Co., USA

SO U.S., 6 pp. Cont.-in-part of U.S. Ser. No. 446,557, abandoned.
CODEN: USXXAM

DT Patent

LA English

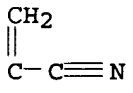
FAN.CNT 2

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 4377444	A	19830322	US 1975-535402	19750113
PRAI	US 1970-29022	A2	19700416		
	US 1971-185721	A1	19711001		
	US 1974-446557	A2	19740227		

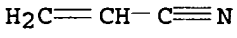
AB Olefinic nitriles are recovered from olefin ammoxidn. product streams containing olefinic nitriles, HCN, MeCN, and carbonyl compds. by feeding the mixture to an **extractive distillation** column with several fractionating trays at a point above the middle of the column, feeding

water as the **extraction** solvent at 60-120°F, removing a **vapor** sidestream at a point below the middle of the column, and stripping HCN, MeCN, and carbonyl compds. from the sidestream. Thus, crude methacrylonitrile (I) [**126-98-7**] from ammoxidn. of isobutylene [115-11-7] was refined to 99.645% purity, yielding a product containing less carbonyl compds. than conventionally purifd. I.

IC B01D003-34
INCL 203096000
CC 35-2 (Chemistry of Synthetic High Polymers)
ST methacrylonitrile purifn; olefin ammoxidn nitrile purifn; isobutylene ammoxidn methacrylonitrile; **extractive distn** sidestream stripping
IT Ammoxidation
(of olefins, purification of olefinic nitriles manufactured by)
IT **Distillation**
(**extractive**, with **vapor** sidestream stripping and recycling, for purification of crude olefinic nitriles)
IT 115-07-1, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(ammoxidn. of, purification of acrylonitrile manufactured by)
IT 115-11-7, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(ammoxidn. of, purification of methacrylonitrile manufactured by)
IT **126-98-7P**
RL: PUR (Purification or recovery); **PREP (Preparation)**
(purification of, from isobutylene ammoxidn. product mixts.)
IT **107-13-1P**, preparation
RL: PUR (Purification or recovery); **PREP (Preparation)**
(purification of, from propylene ammoxidn. product mixts.)
IT **126-98-7P**
RL: PUR (Purification or recovery); **PREP (Preparation)**
(purification of, from isobutylene ammoxidn. product mixts.)
RN 126-98-7 HCAPLUS
CN 2-Propenenitrile, 2-methyl- (9CI) (CA INDEX NAME)



IT **107-13-1P**, preparation
RL: PUR (Purification or recovery); **PREP (Preparation)**
(purification of, from propylene ammoxidn. product mixts.)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)



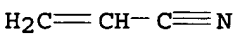
L36 ANSWER 15 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1981:4395 HCAPLUS
DN 94:4395
TI Manufacture of acrylonitrile
PA Asahi Chemical Industry Co., Ltd., Japan
SO Jpn. Kokai Tokkyo Koho, 4 pp.
CODEN: JKXXAF
DT Patent

LA Japanese
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 55104246	A2	19800809	JP 1979-11111	19790202
	JP 61044861	B4	19861004		
PRAI	JP 1979-11111	A	19790202		

AB Acrylonitrile (I) [**107-13-1**]-containing **gaseous** product from ammoxidn. of propylene [115-07-1] was fed into bottom of a cooling tower divided into upper and lower sections into which cooling and stripping **water** was externally recycled sep. as countercurrents to the **gas** mixts. The cooling **water** in the lower section filled with Raschig rings was maintained at 75° so that it absorbed NH3 but not I. The initially cooled **gas** rose to the upper section of 5 trays. The I content in the cooling **water** reached a maximum of 4.5% at the 3rd tray. At this point, the condensate was removed from the tower and fed to **extraction-distillation** tower for further processing. This process provides a min. load on the **extraction-distillation** tower.

IC C07C121-32; C07C120-14
CC 35-2 (Synthetic High Polymers)
Section cross-reference(s): 23
ST acrylonitrile recovery ammoxidn propylene
IT Ammoxidation
(of propylene, to acrylonitrile, product recovery in)
IT 115-07-1, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(ammoxidn. of, to acrylonitrile, product recovery in)
IT **107-13-1P**, preparation
RL: IMF (Industrial manufacture); **PREP (Preparation)**
(manufacture of, by propylene ammoxidn., product recovery in)
IT **107-13-1P**, preparation
RL: IMF (Industrial manufacture); **PREP (Preparation)**
(manufacture of, by propylene ammoxidn., product recovery in)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 16 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1981:3761 HCAPLUS
DN 94:3761
TI Separation of acetonitrile from crude olefinic unsaturated nitriles
IN Katsuta, Issei; Tanaka, Tetsuo
PA Asahi Chemical Industry Co., Ltd., Japan
SO Ger. Offen., 16 pp.
CODEN: GWXXBX
DT Patent
LA German
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	DE 3003319	A1	19800807	DE 1980-3003319	19800130
	DE 3003319	C2	19850314		
	JP 55104244	A2	19800809	JP 1979-11109	19790202
	JP 61044860	B4	19861004		
	GB 2041931	A	19800917	GB 1980-2789	19800128

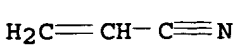
GB 2041931 B2 19830323
US 4294665 A 19811013 US 1980-115865 19800128
PRAI JP 1979-11109 A 19790202
AB An apparatus was developed for separation of MeCN from the crude ammoxidn. products of propene or isobutene by passage through a quenching column, an absorption column (which operated with **H2O**), an **extractive distillation** column for separation of unsatd. nitrile, and a stripping column; the MeCN-containing **vapor** from the stripping column was condensed, regasified, and the MeCN recovered as a liquid via **vapor**-liquid separation
IC C07C121-32; C07C121-18; C07C120-14
CC 23-19 (Aliphatic Compounds)
ST acetonitrile sepn olefinic nitrile
IT **107-13-1P**, preparation
RL: **PREP (Preparation)**
(separation of acetonitrile from crude product mixts. containing)
IT 75-05-8P, preparation
RL: PREP (Preparation)
(separation of, from crude acrylonitrile product mixts.)
IT **107-13-1P**, preparation
RL: **PREP (Preparation)**
(separation of acetonitrile from crude product mixts. containing)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)

L36 ANSWER 17 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1980:472585 HCAPLUS
DN 93:72585
TI Acrylonitrile with low oxazole content
IN Elischer, Stefan; Herberg, Gunther; Lienhard, Klaus; Wagner, Fritz
PA SKW Trostberg A.-G., Fed. Rep. Ger.
SO Ger. Offen., 10 pp.
CODEN: GWXXBX
DT Patent
LA German
FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 2848512	A1	19800522	DE 1978-2848512	19781108
DE 2848512	B2	19801127		
DE 2848512	C3	19811112		
PRAI DE 1978-2848512	A	19781108		

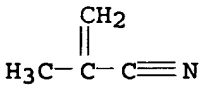
AB Oxazole (I) [288-42-6] content of acrylonitrile (II) [**107-13-1**] from olefin ammoxidn. is reduced to <5 ppm by washing the **gaseous** II product stream with **water** in an absorption column, removing II as overhead from the washed **gas** stream by **distillation** in a solvent **extraction** column, and removing a I-rich side stream from the lower part of the **extraction** column. The **gaseous** side stream is combined with the absorption **water** at the head of the absorption column, and the I is driven off by the residual **gases** at the top of the column and removed with them.
IC C07C121-32; C07C120-14
CC 35-2 (Synthetic High Polymers)
Section cross-reference(s): 23
ST oxazole removal acrylonitrile

IT **107-13-1P**, preparation
RL: PUR (Purification or recovery); **PREP (Preparation)**
(purification of, oxazole removal in)
IT 288-42-6
RL: REM (Removal or disposal); PROC (Process)
(removal of, from acrylonitrile)
IT **107-13-1P**, preparation
RL: PUR (Purification or recovery); **PREP (Preparation)**
(purification of, oxazole removal in)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)

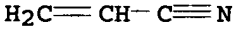


L36 ANSWER 18 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1979:438893 HCAPLUS
DN 91:38893
TI Identification and determination of by-products of the acrylonitrile synthesis
AU Deutsch, K.; Schimke, D.; Neugebauer, B.; Bielicki, K. H.; Stoecker, J.
CS VEB Petrolchem. Komb. Schwedt, Schwedt, DDR-133, Ger. Dem. Rep.
SO Journal fuer Praktische Chemie (Leipzig) (1979), 321(1), 137-40
CODEN: JPCEAO; ISSN: 0021-8383
DT Journal
LA German
AB In the synthesis of H2C:CHCN from MeCH:CH2, NH3, and air in the **gas** phase, using an oxidation catalyst, numerous by-products were formed in addition to the desired products (H2C:CHCN, MeCN, and HCN). These were **extracted** from the waste **waters** of the reactor **gas** quench column and the MeCN removal column, and fractions from **distillation** of the sump and identified by 1H NMR. Among the 44 such compds. identified (and in some cases quant. determined) were, besides the desired products, nicotinonitrile, pyrimidine derivs., fumaronitrile, AcNH2, hydroquinone, Me2CO, PrCN, MeOH, pyridine, PhCN, 2-furancarbonitrile, AcOH, and cyanohydrins of Me2CO, HCHO, and MeCHO.
CC 23-19 (Aliphatic Compounds)
Section cross-reference(s): 80
ST acrylonitrile synthesis byproduct; hydrogen cyanide synthesis byproduct; acetonitrile synthesis byproduct
IT 50-00-0P, preparation 60-35-5P, preparation 64-18-6P, preparation 64-19-7P, preparation 67-56-1P, preparation 67-64-1P, preparation 71-43-2P, preparation 75-07-0P, preparation 75-12-7P, preparation 75-86-5P 78-97-7P 79-06-1P, preparation 79-10-7P, preparation 100-47-0P, preparation 100-54-9P 107-02-8P, preparation 107-12-0P 107-16-4P 109-74-0P 109-75-1P 110-61-2P 110-67-8P 110-86-1P, preparation 123-31-9P, preparation **126-98-7P** 288-42-6P 592-51-8P 617-90-3P 764-42-1P 928-53-0P 1190-76-7P 2478-49-1P 4786-20-3P 5809-59-6P 70688-28-7P 70688-29-8P 70688-30-1P
RL: **PREP (Preparation)**
(by-product from synthesis of acrylonitrile, acetonitrile, and hydrocyanic acid)
IT 289-95-2DP, derivs.
RL: PREP (Preparation)
(by-products from synthesis of acrylonitrile, acetonitrile, and hydrocyanic acid)
IT **107-13-1P**, preparation
RL: **PREP (Preparation)**

(identification and determination of by-products from synthesis of)
IT 70687-56-8P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)
IT 74-90-8P, preparation 75-05-8P, preparation
RL: RCT (Reactant); PREP (Preparation); RACT (Reactant or reagent)
(synthesis of, by-products from)
IT **126-98-7P**
RL: **PREP (Preparation)**
(by-product from synthesis of acrylonitrile, acetonitrile, and hydrocyanic acid)
RN 126-98-7 HCAPLUS
CN 2-Propenenitrile, 2-methyl- (9CI) (CA INDEX NAME)



IT **107-13-1P**, preparation
RL: **PREP (Preparation)**
(identification and determination of by-products from synthesis of)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 19 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1974:52114 HCAPLUS
DN 80:52114
TI Waste treatment process **based** on the submerged combustion technology
AU Tsuruta, Hidemasa
CS Nittetsu Chem. Eng. Ltd., Japan
SO Sekiyu Gakkaishi (1973), 16(8), 646-50
CODEN: SKGSAE; ISSN: 0582-4664
DT Journal
LA Japanese
AB A waste solution (chloride tar) formed during the production of vinyl chloride monomers from C2H4 is incinerated to recover HCl. The waste solution in incinerated in a submerged combustion apparatus, and its waste heat is used to concentrate a CaCl2 solution to .apprx.60%. The resulting **gas** containing .apprx.10% HCl is passed through an absorption column. A 15-18% HCl recovered from the absorption column and the 60% CaCl2 solution are supplied to an **extractive distillation** column, from which a **gas** containing .apprx.60-80% HCl is obtained. A portion of the **gas** is recycled after condensation. The uncondensed HCl **gas** is condensed at .apprx.0° and .apprx.2 kg/cm2 to yield a HCl **gas** containing <50 ppm **H2O**. The effluent **gas** containing HCl 30-50 ppm and Cl2 10-20 ppm from the absorption column is scrubbed with an **alkali** solution and discharged to the atmospheric The recovery of HCl is .apprx.97%. Processes for treating waste solns. containing organic Na salts from caprolactam production and waste solution containing organic compds., cyanides, and (NH4)2SO4 from acrylonitrile production are described.

CC 60-2 (Sewage and Wastes)
Section cross-reference(s): 35
ST hydrogen chloride recovery waste; plastic recovery hydrogen chloride
IT Wastes
(from vinyl chloride manufacture, hydrogen chloride recovery from submerged combustion of)
IT Waste **gases**
(hydrochloride recovery from, from submerged combustion of vinyl chloride manufacture waste)
IT Organic compounds, uses and miscellaneous
RL: REM (Removal or disposal); PROC (Process)
(removal of, from acrylonitrile and caprolactam manufacture effluents)
IT Cyanides, uses and miscellaneous
RL: REM (Removal or disposal); PROC (Process)
(removal of, from acrylonitrile manufacture effluent)
IT Combustion
(submerged, of vinyl chloride manufacture waste, hydrogen chloride recovery from)
IT 7783-20-2P, preparation
RL: PREP (Preparation)
(recovery of, from acrylonitrile manufacture effluent)
IT 7647-01-0P, preparation
RL: PREP (Preparation)
(recovery of, of waste **gas** from submerged combustion of vinyl chloride manufacture waste)
IT 75-01-4P, preparation
RL: IMF (Industrial manufacture); PREP (Preparation)
(waste from manufacture of, hydrochloric acid recovery from submerged combustion of)
IT 105-60-2P, preparation **107-13-1P**, preparation
RL: IMF (Industrial manufacture); **PREP (Preparation)**
(waste from manufacture of, treatment of)
IT **107-13-1P**, preparation
RL: IMF (Industrial manufacture); **PREP (Preparation)**
(waste from manufacture of, treatment of)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)

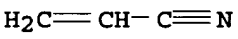
L36 ANSWER 20 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1972:141524 HCAPLUS
DN 76:141524
TI Recovering acrylonitrile, hydrocyanic acid, and acetonitrile from **aqueous** solutions
PA Standard Oil Co.
SO Brit., 4 pp.
CODEN: BRXXAA
DT Patent
LA English
FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI GB 1263213		19720209		
US 3661723		19720000	US	
PRAI JP 1969-40239		19690526		

AB Acrylonitrile [**107-13-1**], hydrocyanic acid [74-90-8], and

acetonitrile [75-05-8] are recovered from their **aqueous** solution(obtained by contacting the product mixture from a catalytic **vapor** phase reaction of propylene, NH3, and mol. O with an acidic solution to neutralize unreacted NH3) by adding CH3CN to bring the CH3CN concentration within the range 0.3-4 weight percent and subsequent **distillation** Thus to an **aqueous** sulfuric acid **extract** containing CH2:CHCN 1.0, CH3CN 0.15, HCN 0.70, and (NH4)2SO4 15 weight percent was added a 20% solution of CH3CN so that the mixture for dist. contained >0.5 weight percent but <10 weight percent CH3CN. A **distillation** column provided with 20 perforated trays gave an overhead composition CH2:CHCN 6, CH3CN 20, HCN 6, and **water** 68 weight percent; the (NH4)2SO4 solution removed at the bottom of the **distillation** column contained <10 ppm CH2:CHCN. Distns. without the addnl. CH3CN gave polymeric deposits at a fast rate, thus fouling the reboiler and the condenser of the **distillation** column.

IC C07C
CC 35 (Synthetic High Polymers)
ST acrylonitrile recovery; acetonitrile recovery; hydrogen cyanide recovery; hydrocanic acid recovery; **distn** recovery acrylonitrile; manuf acrylonitrile
IT 74-90-8P 75-05-8P, preparation **107-13-1P**, preparation
RL: **PREP (Preparation)**
(recovery of, from ammonia-propene reaction mixture)
IT **107-13-1P**, preparation
RL: **PREP (Preparation)**
(recovery of, from ammonia-propene reaction mixture)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)

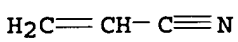


L36 ANSWER 21 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1971:41950 HCAPLUS
DN 74:41950
TI Separating acrylonitrile from acetonitrile in **gaseous** mixtures resulting from the catalytic oxidation of propylene in the presence of ammonia
IN Bitners, Feliks; Brandt, Hans W.; Hausweiler, Arnold; Mayer, Adolf; Beilstein, Gunter M.
PA Erdoelchemie G.m.b.H.; Farbenfabriken Bayer A.-G.
SO Ger. Offen., 12 pp.
CODEN: GWXXBX
DT Patent
LA German
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	DE 1920761	A	19701112	DE 1969-1920761	19690424
	GB 1269195	A	19720406	GB 1970-1269195	19700413
	NL 7005762	A	19701027	NL 1970-5762	19700421
	BE 749500	A	19701026	BE 1970-749500	19700424
	FR 2046509	A5	19710305	FR 1970-15131	19700424
PRAI	DE 1969-1920761	A	19690424		

AB Acetonitrile was separated from an oxidation mixture of propylene with NH3 by **extractive distillation** using a multitray column (95 trays). An **aqueous** washing containing MeCN, HCN, CH2:CHCN, EtCN and **water** was introduced to the 12-25 tray zone of the column which was continuously washed with warm countercurrent **water** to wash

down MeCN and to evaporate other **gaseous** components.
IC C07C
CC 23 (Aliphatic Compounds)
ST sepn acetonitrile; acetonitrile sepn; oxidn propylene; propylene oxidn; acrylonitrile sepn
IT **107-13-1P**, preparation
RL: **PREP (Preparation)**
(from propene, purification in)
IT 75-05-8, uses and miscellaneous
RL: REM (Removal or disposal); PROC (Process)
(removal of, from acrylonitrile)
IT **107-13-1P**, preparation
RL: **PREP (Preparation)**
(from propene, purification in)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)

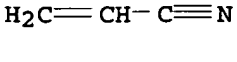


L36 ANSWER 22 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1970:110841 HCAPLUS
DN 72:110841
TI Separation of acrylonitrile and acetonitrile
IN Ikeda, Yoneichi; Takeda, Tsukasa; Hattori, Michio; Kiyomiya, Yutaka
PA Nitto Chemical Industry Co., Ltd.
SO Ger. Offen., 44 pp.
CODEN: GWXXBX
DT Patent
LA German
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	DE 1807654	B2	19740502	DE 1968-1807654	19681107
	DE 1807654	C3	19741219		
	GB 1239460	A	19710714	GB 1968-1239460	19681106
	US 3694322	A	19720926	US 1968-774133	19681107
PRAI	JP 1967-71839	A	19671108		
	JP 1968-28555	A	19680430		

AB An **aqueous** solution of acrylonitrile (I) and MeCN, obtained by known methods of preparing I, is **extractively distilled** with **water** to remove I as **vapor**; the **aqueous** MeCN from the **base** of the column is stream stripped to remove MeCN. The steam stripping is at 1.2-1.6 atmospheric instead of 1 atmospheric Steam from the stripping column is condensed at »100°; the pressure over the condensed liquid (**water** containing 20% MeCN) is reduced to give hot (e.g., 134°) **vapor** and liquid, which are recycled to the bottom and top, resp., of the **extractive distillation** column. Thus, I was separated from MeCN at 1.6 atm in the stripping column. Steam requirements in the **extractive distillation** and steam stripping columns we re 95% and 63%, resp., of amts. required in sepns. in which the stripping column was operated at 1 atmospheric
IC C07C
CC 23 (Aliphatic Compounds)
ST sepn acrylonitrile acetonitrile; acetonitrile sepn acrylonitrile; acrylonitrile acetonitrile sepn
IT **107-13-1P**, preparation
RL: PUR (Purification or recovery); **PREP (Preparation)**

(purification of, acetonitrile removal in)
IT 75-05-8, uses and miscellaneous
RL: REM (Removal or disposal); PROC (Process)
(removal of, from acrylonitrile)
IT **107-13-1P**, preparation
RL: PUR (Purification or recovery); **PREP (Preparation)**
(purification of, acetonitrile removal in)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)

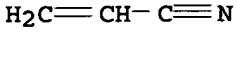


L36 ANSWER 23 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1970:89829 HCAPLUS
DN 72:89829
TI Continuous separation of acrylonitrile and acetonitrile
IN Schoenbeck, Rupert; Krzemicki, Kasimir
PA Lentia G.m.b.H. Chem. und Pharm. Erzeugnisse-Industriebedarf
SO Ger. Offen., 15 pp.
CODEN: GWXXBX
DT Patent
LA German
FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI DE 1920083	A	19700129	DE 1969-1920083	19690421
PRAI DE 1969-1920083	A	19690421		

AB A process is described for continuous separation of MeCN from H2C:CHCN, obtained by reaction of propylene with NH3 and O, by absorption of the **H2O**-soluble product in **H2O**, introduction of the solution into an **extractive distillation** system using **H2O** as the **extracting** agent, obtaining the I-free II at the head of the **extraction distillation** and the I azeotrope as a side stream, and separation of the I azeotrope from most of the **H2O**. The **extractive distillation** was conducted in a plate column and the I side stream was preferably removed above the 15th plate. Thus, a mixture of **H2O** 176, II 135, I 16, N 710, other **gases** 78,and other organic compds. (such as HCN and acrolein) 21 g was charged hourly to the absorption tower, washed with 6000 g **water** containing 5 g I and 17 g other organic compds., and 710 g N and 78 g other **gases** escaped at the top of the column/hr. The mixture at the bottom of the tower, containing II 135, I 21, **H2O** 6176, and other organic compds. 38 g, was heated to 88° and introduced into a 49-plate column 30 plates from the bottom. The column was loaded at the top with 3000 g **water** at 68°. A fraction containing **H2O** 5, II 133, and other organic compds. 15 g was separated/hr. A side stream was separated 20 plates from the bottom at 99° containing **water** 6671, II 2, I 21, and other organic compds. 23 g and conducted to a 30-plate column. At the top of the column at 72°, a mixture consisting of **H2O** 4, II2, I 16, and other organic compds. 1 g was separated/hr. At the **base** of the column, a mixture was separated containing **H2O** 6000 g, I5, and other organic compds. 17 g.
IC C07C
CC 23 (Aliphatic Compounds)
ST acrylonitrile acetonitrile sepn; acetonitrile acrylonitrile sepn
IT **107-13-1P**, preparation
RL: PUR (Purification or recovery); **PREP (Preparation)**

(purification of, acetonitrile removal in)
IT 75-05-8, uses and miscellaneous
RL: REM (Removal or disposal); PROC (Process)
(removal of, from acrylonitrile)
IT **107-13-1P**, preparation
RL: PUR (Purification or recovery); **PREP (Preparation)**
(purification of, acetonitrile removal in)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)

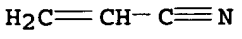


L36 ANSWER 24 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1970:78480 HCAPLUS
DN 72:78480
TI Separation of acrylonitrile and acetonitrile
PA Farbenfabriken Bayer A.-G.; Erdoelchemie G.m.b.H.
SO Fr., 7 pp.
CODEN: FRXXAK
DT Patent
LA French
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	FR 1571726		19690620	FR	
	DE 1618447			DE	
	GB 1218405			GB	
PRAI	DE		19670624		

AB A **gaseous** mixture of MeCN and CH2:CHCN (I) is washed with **water** and I is removed by **extractive distillation** while the MeCN is separated from the **water** by fractional **distillation** The **water** containing any residual MeCN is recirculated to the washing stage. Thus, 54,800 normal l./hr of a **gas** (from the preparation of I by oxidation of propylene in the presence of NH3, containing I 3125, MeCN 320, and HCN 1415 kg) was pumped at 25° into a washing tower containing 45 separator plates. A solution (92,859 kg/hr) containing I 3100, MeCN 320, and HCN 1415 kg was withdrawn at the bottom of the tower, heated to 80°, and pumped into an **extraction** tower containing 72 plates. **Water** at 70° and 30,000 kg/hr was introduced at the head of the tower and steam at 12.7 tons/hr at the **base.** A **gaseous** mixture of I 3100, HCN 1390, **H2O** 2500, and MeCN 0.5kg/hr was withdrawn at the tower head and condensed and a solution of **H2O** 53,368, MeCN 309.5, and HCN 7 kg/hr was withdrawn at the bottom and passed into an **extraction** tower with 6.2 tons/hr steam. A mixture of MeCN 309.5, **H2O** 77.1, and HCN 7 kg/hr was obtained at the head of the **extraction** tower while **water** from the bottom was cooled to 70° and pumped to the top of the **distillation** column, and 70,000 kg/hr **water** containing 10 kg/hr MeCN at 70-100°, from the bottom of the **distillation** tower, was pumped to the washing tower.
IC C07C
CC 23 (Aliphatic Compounds)
ST acrylonitrile acetonitrile sepn; acetonitrile acrylonitrile sepn
IT **107-13-1P**, preparation
RL: **PREP (Preparation)**
(recovery of, from mixts. with acetonitrile)
IT 75-05-8, uses and miscellaneous

RL: USES (Uses)
(separation of, from acrylonitrile)
IT **107-13-1P**, preparation
RL: **PREP (Preparation)**
(recovery of, from mixts. with acetonitrile)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)



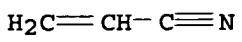
L36 ANSWER 25 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1970:54814 HCAPLUS
DN 72:54814
TI Separation of acrylonitrile from acetonitrile
PA Erdoelchemie G.m.b.H.; Farbenfabriken Bayer A.-G.
SO Fr., 6 pp.
CODEN: FRXXAK
DT Patent
LA French
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	FR 1569457		19690530	FR	
	DE 1618324			DE	
	GB 1239957			GB	
	US 3535849		19700000	US	
PRAI	DE		19670624		

AB Acrylonitrile (I) is separated from the **gaseous** mixture (containing HCN and MeCN as by-products) obtained in the reaction of propylene with NH3. The mixture is washed with hot **water** in a washing column, the **aqueous** solution of I MeCN, and HCN is withdrawn and subjected to **extractive distillation**, I and HCN are **distilled** and the hot **aqueous** MeCN solution residue is divided into 2 streams; the MeCN is recovered from 1 stream by steam stripping, and the other stream is recycled to the top of the washing column. The MeCN in this 2nd stream is entrained by the **gases** (propylene, propane, and carbon oxides) which escape during washing, and the **gas** stream is burned. Thus, a **gas** prepared by the known oxidation of propylene in the presence of N h3 was passed (54,800 standard m3/hr) at 25° into a washing column. The **gas** contained I 3125, MeCN 320, and HCN 1415 kg. An **aqueous** solution (92,679 kg/hr) containing I 3100, MeCN 320, and HCN 1415 k g, taken from the **base** of the column, was heated to 80° and passed into th e midpoint of a 65-plate **extraction** column, where it was contacted with 38 m3/hr hot **water** (obtained from the MeCN/hr was removed from the **base** and separated into 2 streams. One stream (70,000 kg **water** and 180 kg MeCN/hr) was cooled to 50-60° and recycled to the top of the washing column. The other stream (53,538 kg **water**/hr and 139.5 kg MeCN/hr) was passed into an **extraction** column. A mixture of 139.5 kg MeCN/hr and 34.9 kg **water**/hr was **distilled** off. The **water** (38 m3/hr) from the **base** of the column was cooled to 70° and recycled to the top of the column used for the **extractive distillation** of I.

IC C07C
CC 23 (Aliphatic Compounds)
ST acrytonitrile acetonitrile sepn; acetonitrile acrytonitrile sepn
IT **107-13-1P**, preparation

RL: **PREP (Preparation)**
(acetonitrile removal in)
IT 75-05-8, uses and miscellaneous
RL: REM (Removal or disposal); PROC (Process)
(removal of, from acrylonitrile)
IT **107-13-1P**, preparation
RL: **PREP (Preparation)**
(acetonitrile removal in)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)

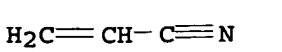


L36 ANSWER 26 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1969:430095 HCAPLUS
DN 71:30095
TI **Extractive distillation** for separating nitrites, peroxides, and their precursors from unsaturated nitriles saturated with **water**
IN Jordan, Jackie B.; White, Thomas R.
PA Standard Oil Co.
SO U.S., 4 pp.
CODEN: USXXAM
DT Patent
LA English
FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI US 3442771	A	19690506	US 1967-661087	19670816
PRAI US 1967-661087	A	19670816		

AB The purpose of this invention is to remove trace nitrite impurities and their precursors from the crude acrylonitrile product obtained from an **extraction distillation** column. The crude nitriles are **distilled** as an azeotropic mixture of the nitrile and **H2O**, both phases of which contain the unwanted impurities. As the **distillate** is partially condensed, an **alkaline alkali** metal salt solution, preferably an **alkali** metal salt of H2CO3, such as a 1-5% solution by weight of Na2CO3, is injected into the **distillate.** This contacts both the organic and **aqueous** phases and exts. the impurities from the organic phase to the **aqueous** phase and there reacts with the impurities. The organic phase, containing the desired nitriles, is drawn off for purification. The trace impurities must be removed from the acrylonitrile solution since these impurities jeopardize many of the polymerization reactions in which the acrylonitrile is used as a monomer.
IC B01D
INCL 203033000
CC 23 (Aliphatic Compounds)
ST acrylonitrile purifn
IT 14797-65-0 14915-07-2, uses and miscellaneous
RL: REM (Removal or disposal); PROC (Process)
(removal of, from acrylonitrile)
IT **107-13-1P**, preparation
RL: **PREP (Preparation)**
(separation of, from nitrite impurities)
IT **107-13-1P**, preparation
RL: **PREP (Preparation)**

(separation of, from nitrite impurities)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)

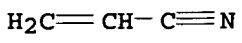


L36 ANSWER 27 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1969:57186 HCAPLUS
DN 70:57186
TI Recovery and purification of acrylate and methacrylate esters by **extractive distillation** with **water**
IN Hougland, John W.; Wisniewski, John C.
PA Standard Oil Co.
SO U.S., 4 pp.
CODEN: USXXAM
DT Patent
LA English
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 3420751	A	19690107	US 1967-624308	19670320
	GB 1222993	A	19710217	GB 1968-1222993	19680220
	FR 1571398	A	19690620	FR 1968-1571398	19680319
PRAI	US 1967-624308	A	19670320		

AB Mixts. containing alcs., unsatd. nitriles, unsatd. acids, **water**, and esters of unsatd. carboxylic acids are separated by **extractive distillation** with **water.** Preferably, the mixture is passed through an ether column, where the desired ester is removed with the side draw, and then through an **extractive distillation** column, from which the ester is removed as overhead in its **water** azeotrope. The overhead from the ether column and the bottoms from the **extractive distillation** column are passed through an alc. column, from which the reflux is partially returned to an esterification reactor and the bottoms, consisting mainly of **water**, is used in the **extractive distillation** The wet ester from the **extractive distillation** is separated in a **decanter** and added at about the middle of a drying column, from which ethers and unsatd. nitriles are withdrawn as overhead and the desired ester, as bottoms containing only a small amount of **water. Water** from the **decanter** is refluxed to the top of the **extractive distillation** column. An example in which Et acrylate was separated from a mixture also containing Et2O, EtOH, acrylonitrile, **water**, acrylic acid, and β-ethoxyethyl propionate was given. This process gives good recovery, and the apparatus requires a min. number of columns and can be used for various mixts.
INCL 203082000
CC 23 (Aliphatic Compounds)
ST ethyl acrylate recovery purifn; acrylate ethyl recovery purifn; recovery purifn ethyl acrylate; purifn recovery ethyl acrylate; **extractive distn** acrylates **water; distn extractive** acrylates **water**
IT 64-17-5P, preparation 79-10-7P, preparation **107-13-1P**, preparation 140-88-5P, preparation
RL: **PREP (Preparation)**
(separation of, from acrylic acid derivs.)
IT 14272-48-1
RL: PROC (Process)

(separation of, from mixts.)
IT **107-13-1P**, preparation
RL: **PREP (Preparation)**
(separation of, from acrylic acid derivs.)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)

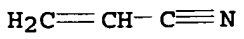


L36 ANSWER 28 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1968:507345 HCAPLUS
DN 69:107345
TI Cellulose copolymers
IN Pesek, Miroslav; Jarkovsky, Jaroslav
SO Czech., 6 pp.
CODEN: CZXXA9
DT Patent
LA Czech
FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI CS 125269		19671215	CS	19660418

AB Polymerization was carried out by irradiation (0.001-20.0 Mev., intensity of irradiation 0.1 r./sec.-500 Mr./sec. and dosing 100 rads-10 megarads) in **H2O** or dilute H2O2. When excess H2O2 was removed the material was treated with **vapors** of vinyl monomer at temps. >40°. Thus, 0.2 g. 1.4-denier viscose staple was treated with 10 cc. 1% H2O2 and after 0.5 hr. the product was irradiated with γ 60Co at 0.362 Mr./hr. to obtain 0.854 megarad. Then excess H2O2 was removed in vacuo, the staple was washed with **distilled H2O**, **H2O** was removed and irradiated staple was introduced into **vapors** on a boiling mixture 1:1 styrene-**H2O** with 0.05% methylene blue for 2 hrs. at 99°. Then the staple was **extracted** with C6H6 for 24 hrs. About 63% of styrene was bound with the activity 98%.
IC C08F
CC 36 (Plastics Manufacture and Processing)
ST cellulose copolymers; styrene cellulose copolymers; vinyl cellulose copolymers
IT Polymerization
(graft, by gamma irradiation, of vinyl compds. on cellulose and rayon)
IT Vinyl compounds, preparation
RL: PREP (Preparation)
(polymers with cellulose and rayon, by gamma irradiation)
IT Gamma rays, chemical and physical effects
(polymerization (graft) by, of vinyl compds. on cellulose and rayon)
IT Rayon, preparation
RL: PREP (Preparation)
(vinyl compound-grafted, by gamma irradiation)
IT 80-62-6P, Methacrylic acid methyl ester, preparation
RL: PREP (Preparation)
(polymers with cellulose and rayon, by gamma irradiation)
IT 79-41-4P, Methacrylic acid, preparation 100-42-5P, Styrene, preparation **107-13-1P**, Acrylonitrile, preparation
RL: **PREP (Preparation)**
(polymers with rayon, graft, by gamma irradiation)
IT 9004-34-6P, preparation

RL: PREP (Preparation)
(vinyl compound-grafted, by gamma irradiation)
IT **107-13-1P**, Acrylonitrile, preparation
RL: **PREP (Preparation)**
(polymers with rayon, graft, by gamma irradiation)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 29 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1968:505946 HCAPLUS
DN 69:105946
TI **Extractive distillation** of unsaturated nitriles
IN Lovett, Gordon H.
PA Monsanto Co.
SO U.S., 8 pp.
CODEN: USXXAM
DT Patent
LA English
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 3399120	A	19680827	US 1965-512651	19651209
	IL 27008	A1	19700521	IL 1966-27008	19661204
	BE 690877	A	19670608	BE 1966-690877	19661208
	NL 6617310	A	19670612	NL 1966-17310	19661209
	ES 334328	A1	19680201	ES 1966-334328	19661209
PRAI	US 1965-512651	A	19651209		

AB An **extractive distillation** process for the recovery of olefinically unsatd. nitriles, especially acrylonitrile (I), from crude nitrile mixts. is described which requires .apprx.33% less steam than a conventional **extractive distillation** process. As in the conventional process, the crude nitrile mixture is fed to a 60-100 tray column. **H2O** is added at the top of the column, causing the **H2O**-miscible impurities to be carried down the column and **H2O**-I to pass overhead. The **H2O**-rich bottoms from the column are passed to a 40-60-tray stripping column where the impurities are taken overhead and condensed, and the **H2O** layer is returned to the column. The column bottoms, mainly **H2O**, are returned to the top of the first column. In the conventional process, both columns are heated with open steam. In the process of this invention, steam is fed only to the bottom of the stripping column in an amount about 10% greater than in the prior art. A portion of the **vapors** from just above the feed point in the stripping column is drawn off and fed to the bottom of the first column. E.g., a stream containing 7.5% I, 1.3% MeCN, 1.3% HCN, and 89.9% **H2O** was fed to the 40th tray of the first column at .apprx.180°F. A mixture of **H2O** and I of the same composition as in the conventional process was taken overhead. Bottoms were fed to the 60th tray of the stripping column. and **vapors** were taken from above the 60th tray and fed below the first tray of the first column. Steam was fed to the bottom of the stripping column at a rate of 6500 lb./hr. compared to 5700 lb./hr. plus 4030 lb./hr., for the first column, in the conventional process.

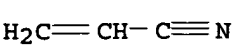
INCL 203084000
CC 23 (Aliphatic Compounds)
ST **ext distn** acrylonitrile; acrylonitrile **ext**

distn; **distn** acrylonitrile **ext**; unsatd nitriles **ext distn**; nitriles **ext distn** unsatd; purifn acrylonitrile

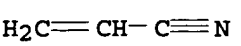
IT **107-13-1P**, preparation
RL: PUR (Purification or recovery); **PREP (Preparation)**
(purification of, apparatus for)

IT **107-13-1P**, preparation
RL: PUR (Purification or recovery); **PREP (Preparation)**
(purification of, apparatus for)

RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)



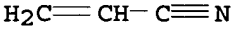
L36 ANSWER 30 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1968:12444 HCAPLUS
DN 68:12444
TI Production of acrylonitrile from propylene
AU Lichtenberger, R.
CS Centre Rech. Lyon, Lyon, Fr.
SO Revue de l'Association Francaise des Techniciens du Petrole (1967), No. 183, 29-35
CODEN: RAFTAX; ISSN: 0004-5470
DT Journal
LA French
AB The Ugine-**Distillers** process is described and compared with other processes for manufacturing CH2:CHCN (I). A mixture of 5-8% by volume C3H6, 5-10% NH3, 10-30% **H2O**, and air is fed over an unspecified catalyst at 400-80°, with a contact time of a few sec. Under optimum conditions the NH3/C3H6 ratio is 1.0-1.2, and 50-60% C3H6 is converted to I, 1-2% to MeCN, 5-7% to HCN, 1-7% to CH2:CHCHO (II), and 16-20% to CO and CO2. The **gaseous** product is washed with H2SO4 to remove NH3, and then with **H2O** to remove organic compds. The cyanohydrin of II and HCN are separated by fractional **distillation**, and MeCN by **extractive distillation** with **H2O**. A flowsheet of the plant is given.
CC 23 (Aliphatic Compounds)
ST ACRYLONITRILE MANUF; PROPYLENE TO ACRYLONITRILE
IT 115-07-1, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(ammoxidn. of)
IT **107-13-1P**, preparation
RL: **PREP (Preparation)**
(manufacture of, from propene)
IT 7664-41-7, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(oxidative, with propene)
IT **107-13-1P**, preparation
RL: **PREP (Preparation)**
(manufacture of, from propene)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 31 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1967:499637 HCAPLUS
DN 67:99637
TI Reclamation of ethylene glycol used in the purification of acrylonitrile
IN Wirtz, Peter; Sennewald, Kurt
PA Knapsack A.-G.
SO Ger., 4 pp. Addn. to Ger. 1189071
CODEN: GWXXAW
DT Patent
LA German
FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 1250427		19670921	DE	19641204

AB Addition to Ger. 1,189,071 (CA 62: 16055h). The reclamation of ethylene glycol (I), used in the purification of crude acrylonitrile (II), is carried out according to a previous patent (loc. cit.) with the modication that p-toluenesulfonic acid (III) catalyst is converted with **water** -free NH3, amine, or alkali or **alkaline** earth hydroxide to the corresponding salt before using it in the decomposition of the addition products of I and Me vinyl ketone (IV) found in the still residue. Thus, to neutralize III present in the distilled residue, NH3 was introduced into the neutralization vessel. A sample of the treated residue treated with **water** had a pH of 7.5. The mixture contained the addition product of I and IV, and NH3 was passed through a preheating arrangement into a distillation **column** and heated to 140°. Within 0.5 min. at 140°/200 mm. the still residue was completely free from IV and any remaining II.
IC C07C
CC 23 (Aliphatic Compounds)
ST ACRYLONITRILE PURIFN; ETHYLENE GLYCOL RECOVERY
IT 18360-27-5P, 2-Propanol, 1,1'-[[2-(2-hydroxyethoxy)ethyl]imino]di-
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)
IT **107-13-1P**, preparation
RL: **PUR (Purification or recovery)**; PREP (Preparation)
(purification of, ethylene glycol recovery from)
IT 107-21-1P, preparation
RL: PREP (Preparation)
(recovery of, during acrylonitrile purification)
IT **107-13-1P**, preparation
RL: **PUR (Purification or recovery)**; PREP (Preparation)
(purification of, ethylene glycol recovery from)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 32 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1961:7793 HCAPLUS
DN 55:7793
OREF 55:1473d-i,1474a-i,1475a-b
TI The mechanism of organomercurial oxidation by mercuric salts
AU Robson, J. H.; Wright, George F.
CS Univ. Toronto
SO Canadian Journal of Chemistry (1960), 38, 1-20

CODEN: CJCHAG; ISSN: 0008-4042
DT Journal
LA Unavailable
AB cf. CA 50, 10015h. The oxidation of certain organomercuric nitrates or acetates by inorg. mercuric salts led to ether, alc., aldehyde, acid, and ester derivs. of the organic compound The observations that the oxidation was inhibited by O, accelerated by acids, yielded esters even in the presence of much **H2O**, that the system polymerized acrylonitrile, and that the same products were formed when pernitrous acid replaced the inorg. salt were evidences of a free radical reaction. Kinetic studies showed that radicals were involved in a self-regenerating chain in which the active monomeric mercurous salt was thought to be the carrier. Oxidation of cyclohexylmercuric nitrate (I) (cyclohexyl = C6H11) by Hg(NO3)2 in MeOH gave 31% C6H11ONO2 (II) and 8% C6H11OMe. I (0.0313 mole) (freshly prepared from the chloromercurial and AgNO3) in 450 ml. dry MeOH was treated with 0.0313 mole of both Hg(NO3)2 and absolute HNO3 38 hrs., cooled to 0°, diluted with 400 ml. **H2O**, 15 ml. 5M NaCl added and the whole filtered to give 12.79 g. CHCl3-insol. HgCl. The filtrate **extracted** with Et2O and the **extract** washed with dilute base and **H2O**, dried, and **distilled** gave a fraction (1.06 g.), b2-3 24-41°, which was chromatographed on silicic acid, eluted with hexane, and analyzed by infrared spectrum. Oxidation of I in **H2O** gave 21% II, 40% C6H11OH (III), and a trace of formylcyclopentane (IV). I (20.00 g.) in 140 ml. **H2O**, stirred 16 hrs. with 18.82 g. Hg(NO3)2 and 7.5 ml. 8M HNO3, was **extracted** with Et2O and 2.51 g. metallic Hg separated from the **aqueous** phase and, by addition of excess NaCl, 24.5 g. HgCl. Et2O exts. washed with dilute base, **H2O**, dried, and **distd** . gave 2 fractions (1) (0.38 g.), b37 15-40°, and (2) (4.14 g.), b42-3 65-84°. Infrared spectra showed the fractions to be nearly identical mixts. of II and III (the OH band at 3450 cm.-1 was used and the covalent nitrate band at 1650 cm.-1). The 2,4-dinitrophenylhydrazine derivative (V) (12 mg.) of IV, m. 149-152°, resulted from treatment of 0.10 g. fraction 2 with dinitrophenylhydrazine (DNPH). Substitution of I by III gave no II under comparable conditions. A similar 10-hr. **aqueous** oxidation of benzylmercuric nitrate (0.0306 mole) gave 2.46 g. yellow oil on concentration of the Et2O exts. A portion (1.000 g.) chromatographed on 2:1 silicic acid-Celite (activated at 150°) gave 2 fractions, (1) (0.360 g.), pos. test for carbonyl and nitrate ester and (2), neg. test for ester. Fraction 1, in 15 ml. dry EtOH, treated 15 hrs. with 1.43 ml. glacial HOAc and 0.59 g. Girard P reagent, poured into 50 ml. cold **H2O** containing 1.19 g. Na2CO3, **extracted** cold with CHCl3, the exts. washed with **H2O**, dried over MgSO4, and concentrated gave 0.288 g. PhCH2ONO2, m. -23 to -17.5°. In an identical oxidation, the oil obtained after Et2O **extraction** was **distilled**; a 2.36 g. fraction, b30 65-100°, showed a trace amount of PhCHO (DNPH), deposited about 20 mg. PhCO2H, and a 0.47 g. sample gave 0.39 g. phenylurethan of PhCH2OH. A suspension, prepared at 0°, of 300 ml. MeOH, 300 ml. **H2O**, 0.06 mole I, 0.009 mole 8M HNO3, and 0.09 mole 90% H2O2 was warmed to and maintained at 25° while 0.066 mole NaNO2 in 60 ml. **H2O** was slowly added in 20 min. The serial addition of like amts. of HNO3, H2O2, and NaNO2 was repeated thrice. The mixture was **extracted** with Et2O, the exts. dried, and **distilled** to give 5.51 g. oil, which gave the V of cyclohexanone (VI), m. 150-3°, and (by infrared spectra) yields of 30% and 25%, resp., III and II. Hg(NO3)2 and H2O2 (0.01 mole each) in 40 ml. dry MeOH gave a neg. Hg+ test after 4 hrs. An exothermic reaction occurred on addition of 3-4 mg. FeSO4.7H2O; after 20 hrs. stirring and addition of 7 ml. 8M HNO3, HgCl and HgO were recovered, with NaCl and NaOH, resp., in 60 and 40% yield. The same procedure in **H2O** produced no Hg+ salt after 10 hrs. Hg(NO3)2 (0.82 millimole) in 5.0 ml. dry MeOH stirred 12 hrs. with 5.0 ml.

0.17M solution of isobutyryl peroxide in MeOH gave a neg. test for peroxide, 0.12 g. HgCl, but no HgO. A series of 10 organomercuric nitrates bleached a MeOH solution of diphenylpicrylhydrazyl (VII), indicating radical formation arising in the organomercurial. Bleaching rates were studied, e.g., 0.005 mole I in 40 ml. MeOH was added to 16.0 mg. VII in 400 ml. MeOH, made up to 500 ml., and % transmittance at 510 mμ measured with time. With mercurial in large excess, 1st-order rates were observed. A rough correlation of relative rates was found between the above 1st-order bleaching rates and the 2nd-order rates of oxidation of the same mercurials with Hg(NO3)2 as in the example. I (0.00313 mole) in 2.5 ml. dry MeOH was added to 0.00313 mole Hg(NO3)2 in 10 ml. MeOH, 0.00626 mole absolute HNO3 added and immediately diluted to 50.00 ml. with MeOH. Aliquots (5.0 ml.) were transferred to tared centrifuge tubes, stoppered, thermostated at 25°, and analyzed by adding 4 ml. 2M HCl, centrifuging after 10 min., washing the precipitate with 5 ml. portions **H2O**, MeOH, and CHCl3, drying the solids at 110° and finally at 56° at 1 mm., and weighing as HgCl. Cyclohexene (VIII) (0.00625 mole) was added to 0.0125 mole HgO and 0.050 mole HNO3 in 23 ml. **H2O**, shaken 5 min., and 0.0125 mole freshly **distilled** acrylonitrile added. Turbidity developed in 40 min. and 0.026 g. polyacrylonitrile (IX) (4% of monomer) was recovered in 3 hrs. The same procedure gave 7% IX in 3 hrs. when the system was deaerated. The same procedure plus 0.65 millimole methylenediacrylamide gave 0.176 g. IX in 3 hrs. These polymers were equivalent to IX from a mixture of 0.01 mole acrylonitrile, 20 ml. **H2O** , 0.10 ml. 90% H2O2, 1-2 mg. FeSO4.7H2O (no visible change in the system in 1 hr.), and 2 ml. 8M HNO3; 0.28 g. IX was obtained in 12 hrs. Treatment of VIII (0.00625 mole) with an equimolar amount of Hg(NO3)2 (from HgO and 1.57 ml. concentrated HNO3) in 23 ml. **H2O** gave a neg. test for Hg++ in 30 min.; addition of 0.0125 mole acrylonitrile gave no measurable amount of IX in 1 day. Reactions of organomercuric acetates with Hg(OAc)2 were much slower than the nitrates but the same type of product was obtained. Peracetic acid (0.05 mole) in CHCl3 added to 0.01 mole cyclohexylmercuric acetate in 20 ml. dry MeOH and refluxed 7 hrs. gave a neg. peroxide test. The amount of HgOAc filtered off and converted to calomel (KCl) was 0.20 g.; the filtrate was diluted to 80 ml. and **extracted** with CHCl3. The **aqueous** phase gave 1.58 g. HgO (NaOH); the CHCl3 phase (**distilled**) gave 0.74 g. VI. Also, α-2-hydroxycyclohexylmercuric acetate oxidized with Fenton's reagent gave 23% IV and 23% 2-chloromercuricyclohexanone (X) (x-ray pattern given). Thus, a system of 0.10 mole VIII, 0.10 mole Hg(OAc)2, and 200 ml. **H2O** gave a neg. test for Hg++ salt after stirring 2 hrs. Over a 2-hr. period, 10 ml. **H2O** containing 0.10 mole H2O2 and 0.10 mole FeSO4.7H2O were added simultaneously and equivalently, the suspension was stirred 68 hrs., **extracted** with Et2O, and the dried exts. **distilled** to give 1.19 g. IV, b. 130-8° (via V, m. 153-5°). The **aqueous** phase was treated with 0.10 mole 5M NaCl, and the precipitate, after drying, **extracted** with 150 ml. CHCl3 to give 7.07 g. CHCl3-soluble solid, m. 138-40° (decomposition). The compound was assumed to be X. Hg(OAc)2 and Hg(NO3)2 in MeOH were reduced to Hg+ (14 and 36%, resp.) in 80-90 hrs. at 50°. Acids, especially BF3.Et2O, catalyzed the reaction. Reduction rates in the system Hg(OAc)2 (0.10M) in MeOH were K = 2.08 + 10-4 and 3.30 + 10-4 min.-1 with BF3.Et2O concns. at 0.02M and 0.04M, resp. Higher acid concns. did not increase the rate. Disappearance of Hg(OAc)2 was determined by volumetric analysis for Hg++ salt with KI and Hg(NO3)2 (the acid interfered with analysis by thiocyanate). The Hg(OAc)2 reduction rate (2.08 + 10-4 with 20 mole-% BF3.Et2O) was not altered in the presence of the methoxymercurials of trans-stilbene (several concns.) and of β,β-dimethylstyrene. Thus, the rate-determining step in the acid-catalyzed oxidation was the oxidation-reduction of the inorg. salt in MeOH. An induction period indicated

radical participation. The influence of O was shown. The system Hg(OAc)2 (0.005 mole) and 0.126 ml. BF3.Et2O in 100 ml. dry MeOH, stirred and maintained at 26-7°, was studied under 17-19 lb. absolute O pressure (rate negligible), under air (K = 1.97 + 10-4 min.-1), and after 4 deaerations (K = 9.28 + 10-4 min.-1). Changes in ultraviolet absorption spectra with time of Hg(NO3)2 and Hg(OAc)2 in MeOH were given both with and without HNO3. 27 references.

CC 10D (Organic Chemistry: Alicyclic Compounds)

IT Alcohols
Aldehydes
Esters
Ethers
(from organomercury compound oxidation)

IT Polymerization
(of acrylonitrile)

IT Oxidation
(of mercury organic compds. by mercuric salts)

IT Reaction kinetics and(or) velocity
(of oxidation, of organomercury compds.)

IT Mercury, 2-methoxycyclohexyl-, nitrate
Mercury, butyl-, nitrate
(kinetics of reactions of)

IT Mercury, benzyl-, nitrate
Mercury, isopropyl-, nitrate
Mercury, propyl-, nitrate
(reaction kinetics of)

IT Mercury, cyclohexyl-
(salts, oxidation of, mechanism of)

IT Mercury, (2-methoxy-1,2-diphenylethyl)-
Mercury, [α-(1-methoxy-1-methylethyl)benzyl]-
(salts, reaction kinetics of)

IT 7439-97-6, Mercury
(compds., oxidation by Hg(II) salts, mechanism of)

IT 100-52-7, Benzaldehyde
(formation of, from benzylmercury nitrate oxidation)

IT 108-94-1, Cyclohexanone 2108-66-9, Cyclohexyl nitrate
(formation of, from cyclohexylmercury nitrate)

IT 15285-42-4, Benzyl nitrate
(from benzylmercury nitrate oxidation)

IT 872-53-7, Cyclopentanecarboxaldehyde 931-56-6, Ether, cyclohexyl methyl
(from cyclohexylmercury nitrate oxidation)

IT 62-53-3, Aniline 100-46-9, Benzylamine **107-15-3**, Ethylenediamine 124-09-4, 1,6-Hexanediamine 7664-41-7, Ammonia 90952-94-6, Cyclohexanol, 2-(acetoxymercuri)-
(oxidation of)

IT **107-13-1**, Acrylonitrile
(polymerization of)

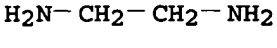
IT 14839-64-6, Mercury, 2-oxocyclohexyl-, chloride 14839-64-6, Cyclohexanone, 2-(chloromercuri)-
(preparation of)

IT 7439-97-6, Mercury
(salts, organomercury compound oxidation by)

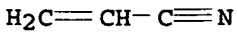
IT **107-15-3**, Ethylenediamine
(oxidation of)

RN 107-15-3 HCAPLUS

CN 1,2-Ethanediamine (9CI) (CA INDEX NAME)



IT **107-13-1**, Acrylonitrile
(polymerization of)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 33 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1960:7169 HCAPLUS
DN 54:7169
OREF 54:1489b-i,1490a-i,1491a-f
TI The addition of acrylonitrile to pyrroles
AU Fischer, Hans; Loewe, Heinz
CS Tech. Hochschule, Munich, Germany
SO Ann. (1958), 615, 124-36
DT Journal
LA Unavailable
AB This is a study of the addition of acrylonitrile to pyrrole derivs. in order to make various pyrrolepropionic acids, with Na alcoholates as catalyst. Acrylonitrile was added to 2,4-dimethyl-5-carbethoxypyrrole to form 2,4-dimethyl-5-carbethoxy-1-pyrrolepropionitrile; nucleus substitution of this was investigated. Certain condensation reactions and the saponification of the nitrile group were investigated. The behavior of the new pyrrole derivs. which were obtained from 2,4-dimethyl-5-carbethoxypyrrole was given. The following 1-pyrrolepropionitriles were obtained by addition of acrylonitrile: 2,4-dimethyl-5-carbethoxy- (I), 2,4-dimethyl-3-formyl-5-carbethoxy- (II), 2,4-dimethyl-3,5-dicarbethoxy- (III), 2,4-dimethyl-3-acetyl-5-carbethoxy- (IV), 2,3-dimethyl-5-formyl-4-carbethoxy- (V) 2,3-dimethyl-5-carbethoxy- (VI), 2-methyl-5-carbethoxy- (VII), 2-methyl-3-carbethoxy- (VIII), 2,4-dimethyl-3-ethyl-(IX), 2,4-dimethyl- (X), 2,4-dimethyl-5-carbethoxy-3-{β-[carbethoxy(2-cyanoethyl)amino]athyl}- (XI). Acrylonitrile could not be added to 2,4-dimethyl-5-carbethoxy-3-pyrrolepropionic acid and to 2,4-dimethyl-5-carbethoxy-3-nitrovinyl)pyrrole. Rearrangement of the propionitrile residue from N to C did not take place. Under the action of sodium alcoholate at 150° the propionitirle residue was again split out. II showed the normal reaction of pyrrole aldehyde unsubstituted on the N. It gave an oxime, a semicarbazone, a phenylhydrazone, and an azlactone, condensed with malonic acid to 2,4-dimethyl-5-carbethoxy-1-(β-cyanoethyl)-3-pyrroleacrylic acid (XII), reduced to the propionic acid analog (XIII) and condensed with nitro-methane to 2,4-dimethyl-5-carbethoxy-3-(2-nitrovinyl)-1-pyrrolepropionitrile (XIV), which was converted into XIV 3-(β-hydroxyiminoethyl) analog (XV) and then with Ac2O into XIV 3-cyanomethyl analog (XVI). II aldoxime gave with Ac2O the acetylated oxime, while the corresponding material with the unsubstituted N was converted smoothly into the nitrile. The 1-(p-tolyl) analog of these aldoximes was only converted into the ecetyl compound 2,4-Dimethyl-5-carbethoxypyrrole (7.5 g.) is dissolved in 10 cc. freshly **distilled** acrylonitrile and colled to give a stiff pate. Into the colled mass was added dropwise 10 cc. 5% NaOEt in absolute alc., with shaking until small bubbles appeared. The mixture was colled, after 1 hr. triturated with 50 cc. Et2O, the solid filtered off and exhaustively **extracted** with Et2O, dried, evaporated, and the residue fractionated to give β-ethoxypropionitrile, b10 61-3°, 2,4-dimethyl-5-carbethoxypyrrole, b10 130-50°, and I, b10 175-85°. I, obtained in 50-80% yield, m. 84.5° (MeOH). I (0.8 g.) heated 10

hrs. in a pressure tube at 150° with 4 cc. 7.5% NaOMe in absolute alc. gave 2,4-dimethyl-5-carbethoxypyrrole, m. 123° (alc.). The same results were obtained with 1-propionamide analog. I (1.5 g.) in 5 cc. glacial AcOH treated with 0.3 cc. Br in 2 cc. glacial AcOH yielded 1.5 g. 3-bromo-2,4-dimethyl-5-carbethoxy-1-pyrrolepropionitrile m. 85-8° (EtOH). I (18 g.) was suspended in 75 cc. absolute Et2O and 25 cc. CHCl3; for removal of alc. the mixture was shaken with **water** and dried over P2O5. After addition of 10 cc. anhydrous HCN the mixture was saturated with dried HCl, while cooling with salt and ice. The mixture was chilled overnight to give the imine hydrochloride of the aldehyde, which was hydrolyzed with ice **water** to give 15 g. II, m. 106° (alc.), also prepared by addition of acrylonitrile to 2,4-dimethyl-3-formyl-5-carbethoxypyrrole; oxime m. 142° (MeOH); N-Ac derivative of the oxime, m. 118° (alc.); semicarbazone m. 210-11°; phenylhydrazone m. 128° (EtOH); azlactone, yellow plates, m. 147° (EtOH). 2,4-Dimethyl-5-carbethoxy-1-pyrrolepropionamide (0.5 g.) in 10 cc. absolute Et2O with 0.3 cc. HCN and HCl **gas** gave 2,4-dimethyl-3-formyl-5-carbethoxy-1-pyrrolepropionamide, m. 188° (alc.). II (0.5 g.) was stirred with 5 cc. of 7.5% NaOEt in absolute alc., 0.3 cc. hydrazine hydrate was added and heated in pressure tube 10 hrs. at 160-70° to give 2,3,4-trimethylpyrrole, m. 36°; picrate m. 140-2° (alc.). I (0.6 g.) in 1 cc. hot Ac2O was treated with SnCl2.2H2O to give 0.2 g. IV, m. 76° (alc.). 2,4-Dimethyl-3-acetyl-5-carbethoxy-1-pyrrolepropionamide, obtained from 0.6 g. 2,4-dimethyl-5-carbethoxy-1-pyrrolepropionamide with Ac2O by a process analogous to that for preparation of IV, m. 167° (MeOH). IV was also prepared by addition of acrylonitrile to 2,4-dimethyl-3-acetyl-5-carbethoxypyrrole. 2,3-Dimethyl-4-carbethoxy-1-pyrrole-5-carboxaldehyde (1 g.) with acrylonitrile gave 0.9 g. V, yellow needles, m. 114° (alc.). 2,4-Dimethyl-3,5-dicarbethoxypyrrole (1 g.) with acrylonitrile gave 0.8 g. III, m. 106° (alc.). III (0.5 g.) heated with 3 cc. 7.5% NaOEt in absolute alc. in a pressure tube 10 hrs. at 150° gave by recrystn. 2,4-dimethyl-3,5-dicarbethoxypyrrole, m. 132°. VI (0.9 g.) was obtained from 1 g. 2,3-dimethyl-5-carbethoxypyrrole, m. 63° (alc.). 2-Methyl-5-carbethoxypyrrole gave VII, m. 58° (alc.); 2-methyl-3-carbethoxypyrrole gave VIII, m. 93° (alc.). 2,4-Dimethyl-3-ethylpyrrole (5 cc.) gave 3 g. IX, b0.2 130°; picrate m. 185° (alc.). Freshly **distilled** 2,4-dimethylpyrrole (5 g.) and acrylonitrile gave 3 g. X, yellow oil, b11 149°. A similar reaction gave XI, m. 101°.

2,4-Dimethyl-5-carboxy-1-pyrrolepropionic acid amide (XIV). I (5 g.) in 8 cc. alc. and a solution of 5 g. KOH and 10 cc. **water** was heated to boiling on **water** bath, whereby NH3 began to evolve. After some time, also in the heat, the resulting precipitate of K salt was separated, washed, dissolved in **H2O**, and the solution acidified with dilute AcOH to give 1.2 g. (purified) 2,4-dimethyl-5-carboxy-1-pyrrolepropionamide (XVII), m. 195° (Me2CO); Me ester m. 166° (MeOH). I (5 g.) was heated to boiling for 10 hrs. in 8 cc. alc. and 5 g. KOH in 10 cc. **water**. The first separated K salt of XVII redissolved for the greater part. The mixture was filtered, the filtrate cooled to 0° and 2 g. 2,4-dimethyl-5-carboxy-1-pyrrolepropionic acid (XVIII) precipitated by careful acidification with AcOH, 90-100° (decomposition). Decomposition of XVIII by heating gave 2,4-dimethyl-1-ethylpyrrole; picrate not m. below 300°, further heating caused detonation. I (3 g.) in 30 cc. absolute Et2O and 3 cc. absolute alc. was cooled with ice and salt and saturated with anhydrous HCl to give the imide hydrochloride of Et 2,4-dimethyl-5-carbethoxy-1-pyrrolepropionate (XIX). Hydrolysis with ice **water** gave XIX, oil, b11 178°. I (0.6 g.) was added to 10 cc. of mixture of equal parts of HI (d. 1.70) and glacial AcOH and heated 2 hrs. on the boiling **water** bath. The dark brown solution was decolorized with granular Ph4I and the solvent was evaporated in a vacuum on the **water** bath.

NaOAc solution was added to the residue to neutralize the HI. The residue was crystallized to yield 0.4 g. 2,4-dimethyl-5-carbethoxy-1-pyrrolepropionamide (XX) m. 159° (alc.). Saponification with **aqueous** alc. KOH gave XVII. XIX (1 g.) was added to 10 cc. of a concentrated solution of NH3 in absolute alc. and allowed to stand closed for 1 week. The solution was evaporated and the residue recrystd. from alc. to give XX. Equal parts of XX and P2O5 heated at 200° in a vacuum gave I. II (1 g.) was dissolved in 10 cc. alc., 0.8 g. malonic acid and 0.7 cc. freshly **distilled** aniline was added, and the mixture heated 12 hrs. on boiling **water** bath to give 1.2 g. XII, m. 186° (CHCl3). XII was dissolved in 10% NaOH solution and within 6 hrs., with stirring, excess 3% Na-Hg was added. The temperature was held between 12 and 15°, and from time to time enough dilute HCl was added so that turbidity resulted. In this manner the saponification of the carbethoxy residue by the developing **alkalinity** was avoided. After removal of the mixed greases with Et2O the **watery** layer was cooled to 0°, acidified cautiously with dilute AcOH just to an acid reaction; the precipitate was immediately filtered off and dried on an unglazed plate to yield 70% XIII, pink, m. 133° (alc.). II (1 g.) was dissolved in 4 cc. absolute alc., then 1 cc. MeNO2 and 0.05 cc. 20% MeNH2 in absolute alc. was added and the mixture heated to boiling on the **water** bath to give 0.8 g. gold-yellow XIV, m. 145° (alc.). XIV (3 g.) was finely powdered and slurried in 100 cc. dry Et2O and 3 g. Al-Hg was added in several portions with frequent shaking. The reduction was held in process through the repeated addition of several drops of **water.** It was allowed to stand overnight, filtered and the slime **extracted** with Et2O. The combined exts. were dried with Na2SO4 and the solvent evaporated The residue was recrystd. from acetone to yield 30 to 40% XV, m. 166°. XV (0.2 g.) was dissolved in 4 cc. Ac2O then 0.4 g. anhydrous NaOAc was added and heated 2 hrs. on the boiling **water** bath; then 25 cc. **water** was added. After several hrs. XVI separated, m. 90° (alc.). 2-Methyl-3-formyl-5-carbethoxypyrrole (5 g.) was heated 2 hrs. on a boiling **water** bath in 20 cc. absolute alc. with 3 cc. nitromethane and 0.5 cc. of a 20% solution of methylamine in absolute alc. to give 70% yellow 2-methyl-3-(2-nitrovinyl)-5-carbethoxypyrrole (XXI), m. 195° (alc.). Reduction of XXII with Al-Hg gave 30% 2-methyl-5-carbethoxypyrrole 3-acetaldoxime (XXII), m. 158-61° (alc.). A suspension of 10 g. 2-methyl-5-carbethoxypyrrole in 20 cc. absolute Et2O and 20 cc. alc.-free dried CHCl3 and 8 g. NCCO2Et was cooled in ice-salt, saturated with dry HCl, and allowed to stand overnight in the cold to give a quant. yield of the imide-HCl of Et 2-methyl-5-carbethoxy-3-pyrroleglyoxylate (XXIII). The imide hydrochloride stirred in 400 cc. of ice **water** gave after several hrs. XXIII, m. 160° (alc.); phenylhydrazone, yellow, m. 144° (alc.); hydrazide (XXIV) m. 197°; benzoylhydrazide m. 248°. XXIII (1 g.) with 7 cc. 7.5% NaOEt heated with 0.5 cc. hydrazine hydrate 10 hrs. at 165-70° gave the very labile 2-methylpyrrole-5-carboxylic acid-3-acetic acid which was not isolated, but was treated with CH2N2 in Et2O to give 50 mg. Me 2-methyl-5-carbomethoxy-3-pyrroleacetate (XXV), m. 103° (alc.). Et 2-methyl-5-carbethoxy-3-pyrrolepropionate (XXVI), 60% from 5 g. 2-methyl-5-carbethoxy-3-pyrrolepropionic acid in 50 cc. of a saturated solution of HCl in absolute alc., m. 65° (alc.). XXVI (5 g.) heated 2 hrs. on a boiling **water** bath in 10 cc. alc. with 2 cc. hydrazine hydrate gave a mixture of the hydrochloride of 2-methyl-5-carbethoxy-3-pyrrolepropionic acid hydrazide and N2H4.HCl. 2-Methyl-5-carbethoxy-3-pyrrolepropionic acid azide. This mixture was dissolved in 10 times the amount of **water** and filtered from undissolved material. The solution was cooled with ice and an ice cold 10% solution of NaNO2 in excess was added carefully. The azide precipitated crystalline and was used without purification. The completely dried crude azide was dissolved in 10 times the amount of absolute

alc. and heated to boiling on the **water** bath; N actively evolved. After 3 hrs. the alc. was evaporated and the urethan recrystd. from absolute alc. to give 0.5 g. Et (2-methyl-5-carbethoxy-3-pyrryl)ethylcarbamate (XXVII), m. 120° (alc.). 2-Methyl-5-carbethoxy-3-pyrrolepropionic acid (1 g.) was heated to boiling in 10 cc. glacial AcOH with 1.4 g. pure, completely dried bromomalonic acid. After 5 min. 10 cc. hot **water** was added and the solution allowed to cool to give by repeated crystallization from AcOH and **water** 1 g. brown 4-bromo-2-methyl-5-carbethoxy-3-pyrrolepropionic acid, m. 180° (decomposition). 2,3-Dimethyl-5-carbethoxypyrrole (0.2 g.) in 2 cc. glacial AcOH and 0.3 g. pure and completely dried bromomalonic acid gave from glacial AcOH and **water** 0.2 g. brown needles of 4-bromo-2,3-dimethyl-5-carbethoxypyrrole, m. 152° (decomposition). 4-Bromo-2,3-dimethyl-5-pyrrolecarboxylic acid azide (0.2 g.) was prepared from 0.2 g. 2,3-dimethyl-5-pyrrolecarboxylic acid azide and 0.3 g. bromomalonic acid, brown needles, m. 145° (decomposition) (glacial AcOH and **water**).

CC 10G (Organic Chemistry: Heterocyclic Compounds)

IT Rearrangements
(of pyrrole-1-propionitrile derivs.)

IT Cyanoethylation
(of pyrroles)

IT 53451-57-3, 2-Selenophenecarboxaldehyde, 5-nitro- 57500-58-0, 2-Selenophenecarboxaldehyde, 4-nitro- 103386-46-5, Pyrrole-2-carboxylic acid, 1-(2-carbamoylethyl)-3,5-dimethyl-
(and derivs.)

IT 2199-44-2, Pyrrole-2-carboxylic acid, 3,5-dimethyl-, ethyl ester
(and its cyanoethylation)

IT 14306-10-6, Pyrrole-2-carboxylic acid, 3,5-dimethyl-4-(2-nitrovinyl)-, ethyl ester 37789-64-3, Pyrrole-3-propionic acid, 5-carboxy-2,4-dimethyl-, 5-ethyl ester
(cyanoethylation of)

IT 857201-02-6, Pyrrole-3-glyoxylic acid, 5-carboxy-2-methyl- 857202-10-9, Pyrrole-2-carboxylic acid, 1-(2-carbamoylethyl)-4-formyl-3,5-dimethyl- 857204-81-0, Pyrrole-2-carboxylic acid, 1-(2-cyanoethyl)-4-formyl-3,5-dimethyl- 858027-49-3, Pyrrole-3-propionic acid, 5-carboxy-2-methyl-
(derivs.)

IT 109-97-7, Pyrrole
(derivs., cyanoethylation of)

IT 1466-76-8, Benzoic acid, 2,6-dimethoxy- 2141-62-0, Propionitrile, 3-ethoxy- 2436-79-5, Pyrrole-2,4-dicarboxylic acid, 3,5-dimethyl-, diethyl ester 3855-78-5, Pyrrole, 2,3,4-trimethyl- 53871-28-6, Pyrrole, 1-ethyl-2,4-dimethyl- 98550-56-2, Pyrrole-2-carbonyl azide, 3-bromo-4,5-dimethyl- 99069-04-2, Pyrrole-2-carboxylic acid, 5-methyl-4-(2-nitrovinyl)-, ethyl ester 99076-49-0, Pyrrole-1-propionic acid, 2-carboxy-3,5-dimethyl- 99362-09-1, Pyrrole-1-propionitrile, 2,4-dimethyl- 100057-91-8, Pyrrole-2-carboxylic acid, 4-[2-(azidoformyl)ethyl]-5-methyl-, ethyl ester 100129-25-7, Pyrrole-3-propionic acid, 4-bromo-5-carboxy-2-methyl-, 5-ethyl ester 100387-91-5, Pyrrole-2-carboxylic acid, 4-bromo-1-(2-cyanoethyl)-3,5-dimethyl-, ethyl ester 100720-06-7, Pyrrole-2-carboxylic acid, 1-(2-cyanoethyl)-4-(cyanomethyl)-3,5-dimethyl-, ethyl ester 100720-50-1, Pyrrole-2-carboxylic acid, 1-(2-cyanoethyl)-3,5-dimethyl-4-(2-nitrovinyl)-, ethyl ester 100723-41-9, Pyrrole-2-carboxylic acid, 4-acetyl-1-(2-cyanoethyl)-3,5-dimethyl-, ethyl ester 100797-07-7, Pyrrole, 2,3,4-trimethyl-, picrate 100801-06-7, Pyrrole-2-carboxylic acid, 4-(2-carboxyaminoethyl)-5-methyl-, diethyl ester 100876-64-0, Pyrrole-2-carboxylic acid, 4-acetyl-1-(2-carbamoylethyl)-3,5-dimethyl-, ethyl ester 100958-54-1, Pyrrole-3-acrylic acid, 5-carboxy-1-(2-cyanoethyl)-2,4-dimethyl-, 5-ethyl ester 101117-13-9,

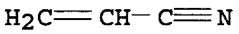
Pyrrole-2-carboxylic acid, 1-(2-cyanoethyl)-4-(formylmethyl)-3,5-dimethyl-, ethyl ester, oxime 101257-49-2, Pyrrole-3-acetic acid, 5-carboxy-2-methyl- 101496-90-6, Pyrrole-3-propionic acid, 5-carboxy-1-(2-cyanoethyl)-2,4-dimethyl-, 5-ethyl ester 101580-02-3, Pyrrole-1-propionitrile, 3-ethyl-2,4-dimethyl- 101580-03-4, Pyrrole-1-propionitrile, 3-ethyl-2,4-dimethyl-, picrate 101879-23-6, Hydrazine, 1-benzoyl-2-[(5-carboxy-2-methylpyrrol-3-yl)glyoxyloyl]-, ethyl ester 102236-53-3, Pyrrole-2-carboxylic acid, 3-bromo-4,5-dimethyl-, ethyl ester 102459-97-2, Pyrrole-2-carboxylic acid, 1-(2-cyanoethyl)-3,5-dimethyl-4-[(5-oxo-2-phenyl-2-oxazolin-4-ylidene)methyl]-, ethyl ester 103095-40-5, Pyrrole-3-acetic acid, 5-carboxy-2-methyl-, dimethyl ester 103386-48-7, Pyrrole-2-carboxylic acid, 4-(formylmethyl)-5-methyl-, ethyl ester, oxime 103853-68-5, Pyrrole-3-carboxylic acid, 1-(2-cyanoethyl)-2-methyl-, ethyl ester 103855-57-8, Pyrrole-2-carboxylic acid, 1-(2-cyanoethyl)-5-methyl-, ethyl ester 103990-79-0, Pyrrole-2-carboxylic acid, 4-[2-[carboxy(2-cyanoethyl)amino]ethyl]-1-(2-cyanoethyl)-3,5-dimethyl-, diethyl ester 105336-91-2, Pyrrole-2-carboxylic acid, 1-(2-cyanoethyl)-4,5-dimethyl-, ethyl ester 105337-45-9, Pyrrole-2-carboxylic acid, 1-(2-cyanoethyl)-3,5-dimethyl-, ethyl ester 107418-00-8, Pyrrole-2,4-dicarboxylic acid, 1-(2-cyanoethyl)-3,5-dimethyl-, diethyl ester 107682-89-3, Pyrrole, 1-ethyl-2,4-dimethyl-, picrate 108482-19-5, Pyrrole-3-acetic acid, 5-carboxy-α-imino-2-methyl-, diethyl ester, hydrochloride 108953-98-6, Pyrrole-2-carboxylic acid, 1-(2-cyanoethyl)-4-formimidoyl-3,5-dimethyl-, ethyl ester, hydrochloride 109366-54-3, Pyrrole-2-carboxylic acid, 1-[2-(1-ethoxyformimidoyl)ethyl]-3,5-dimethyl-, ethyl ester, hydrochloride 109366-54-3, Pyrrole-1-propionimidic acid, 2-carboxy-3,5-dimethyl-, diethyl ester, hydrochloride 109394-74-3, Pyrrole-1-propionic acid, 2-carboxy-3,5-dimethyl-, diethyl ester 113324-72-4, Pyrrole-3-carboxylic acid, 1-(2-cyanoethyl)-2-formyl-4,5-dimethyl-, ethyl ester
(preparation of)

IT **107-13-1**, Acrylonitrile
(reaction of, with pyrrole derivs.)

IT **107-13-1**, Acrylonitrile
(reaction of, with pyrrole derivs.)

RN 107-13-1 HCAPLUS

CN 2-Propenenitrile (9CI) (CA INDEX NAME)



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OREF 53:10111c-i,10112a-i,10113a-c

TI Pyrolysis. XIII. Competitive alkyl-O and acyl-O scission in the pyrolysis of esters; α,α-disubstituted cyanomethyl carboxylates

AU Bennett, R. N.; Deans, A. A.; Harris, J. G. H.; Ritchie, P. D.; Shim, J. S.

CS Roy. Coll. Sci. Technol., Glasgow, UK

SO Journal of the Chemical Society, Abstracts (1958) 4508-15
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DT Journal

LA Unavailable

AB cf. C.A. 52, 9973c. New evidence, coupled with a survey of the literature, shows that the well-known alkyl-oxygen scission of carboxylic esters to carboxylic acid plus alkene (**vapor** phase, about

400-500°) occurs in competition with a less familiar acyl-O scission by what is essentially a retro-Tishehenko reaction. The molar ratio of these 2 primary routes can vary over a wide range, with alkyl-O and acyl-O scission as the extreme limiting cases. Factors governing the balance between them are discussed, and the occurrence of further reactions is briefly noted. To show that a primary competition between alkyl-O and acyl-O scission exists, with subsequent secondary breakdown of some of the primary products, and to test the general validity of the concept, six 1-cyanoalkyl and 1-cyanocycloalkyl esters were studied. These were: BzOCMe2CN (I), BzOCMeEtCN (II), AcOC-MeEtCN (III), X(OBz)CN (X = cyclopentylidene) (IV), X(OBz)CN (X = cyclohexylidene) (V), and X(OBz)CN (X = cycloheptylidene) (VI). The results fully confirm the idea of competition between the 2 scissions where both are structurally permissible. All 6 esters, which each contain at least one β-H atom, undergo a major A' scission (90%) with a competing minor B2 scission (up to 10%). At high temps. used (500°), acyl cyanide from the B2 reaction is too unstable to survive in the pyrolyzate, but in each case its known breakdown products are observed, sometimes together with further minor secondary products. Three different flow-vessels were used, P 1, P 2 (borosilicate glass), and S (stainless steel). All were packed with borosilicate glass tubing, the free unpacked space being 125, 50, and 80 ml., resp. Two tables summarized the general conditions and results from 14 runs. Apparent losses in weight are due to carbonization and (or) holdup in the packed vessel. The examination of typical pyrolyzates is given below. HCN was removed from exit **gases** by a cold trap, and ketene by a PhNH2-Et2O trap. Aldehydes and ketones are characterized by their 2,4-dinitrophenylhydrazones, benzene as m-dinitrobenzene, and PhCN by conversion to benzamide. I is obtained in 42% yield as an oil, b70 184-5°, solidifying to crystals, m. 36°. The following data are obtained (compound pyrolyzed, run number, reaction vessel, temperature, feed rate in g./min., contact time in sec., weight of pyrolyzed g., g. in main receiver, l. of **gaseous** pyrolyzate, % composition of CO, CO2, unsatd. hydrocarbons, composition of total pyrolyzate BzOH, olefinic nitrile, ketone, benzonitrile, C6H6, unchanged pyrolyzant, HCN, and processing losses, tars, **gases**, etc., given): I, 1, S, 400°, 1.46, 11, 90.7, 82.4, 5.6, 11, 89, nil, present (p), (p), (p), (p), (p), -, -, -; II, 2, S, 510°, 1.25, 12, 100.0, -, 0.5, (p), (p), -, (p), (p), (p), (p), -, -, -, -; IV, 10, P 2, 495°, 0.60, 17, 69.0, 67.2, 1.5, 25, 75, nil, 32.0, 22.5, 1.2, 1.8, 3.0, nil, (0.7), 8.5; V, 11, P 2, 395°, 0.60, 21, 63.0, 61.0, -, -, -, -, 17.6, 14.7, 8.7, 9.7, nil, 2.8, (0.1), 9.5; V, 12, P 2, 495°, 0.80, 16, 76.0, 71, 4.0, 11, 88, 1, 31.0, 25.5, 2.0, 1.8, 0.8, nil, (0.1), 14.9; V, 13, P 2, 555°, 0.50, 20, 49.0, 47.2,-, -, -, -, 20.3, 18.2, 0.8, 0.7, 0.4, nil, (0.2), 8.6; VI, 14, P 2,495°, 0.43, 27, 64.0, 63.0, 1.2, 26, 74, nil, 17.7, 18.0, 8.6, 7.5, 0.3, nil, (0.3), 11.9. For III the following results were obtained (run number, reaction vessel, temperature, feed rate g./min., contact time in sec., weight pyrolyzed in g., (a) g. in main receiver, (b) **gaseous** products, % composition of (b) CO, CO2, unsatd, hydrocarbons, saturated hydrocarbons, composition of total pyrolyzate in g. AcOH by titration, by fractionation, b. 112-16° total, nitrile, b. 117-19° total, nitriles, b. 120-4°, total, nitrile, b. below 92° mostly MeCOEt, unchanged pyrolyzant, HCN given): 3, P 1, 425°, 2.0, 9, 100.0, 99.9, 2.9, -, -, -, -, 40.7, 38.1, 23.0, 20.2, 6.8, 6.5, 11.6, 10.4, 4.2, 3.0, 0.01; 4, P 1,425°, 3.3, 6, 100.0, 99.7, 2.2, 38, 2, nil, 60, 41.2, 37.9, 10.2, 8.6, 11.9, 11.6, 18.3, 16.5, 3.1, 1.5, trace; 5, P 1, 425°, 9.7, 2, 100.0, 99.6, 2.0, 31, nil, nil, 69, 37.5, 42.1, 16.8, 14.4, 2.8, 1.7, 17.7, 16.0, 3.2, 9.5, trace; 6, P. 1, 475°, 2.5, 2.5, 7, 100.0, 88.5, -, -, -, -, -, -, 40.3, 26.2, 24.0, nil, nil, 8.2, 7.6, 0.2, 3.0, 0.02; 7, P 1, 475°, 4.4, 4, 100.0, 95.2, 1.4, 65, 6, 4, 25, -, 38.5, 24.1, 20.8, nil, nil, 5.7, 5.5, 0.2,

1.0, 0.01; 8, P 1, 475°, 10.9, 2, 100.0, 98.5, 2.6, 52, 1, 2, 45, 39.0, 40.5, 16.3, 12.3, 12.5, 11.7, 8.1, 6.2, 2.4, 4.0, 0.01; 9, P 1, 525°, 4.4, 4, 100.0, 91.6, 2.7, 51, 12, 7, 30, 39.9, 39.3, 11.6, 10.0, 2.1, 1.2, 15.6, 15.1, 3.8, 1.0, 0.01. Run 1. No HCN could be detected. **Distillation** of (a) gave a trace of Me2CO, 44 g. substance, b. 70-95°, and a solid residue. The 44 g. fraction gave C6H6, α-methylacrylonitrile, b. 91-1.5°, and the residue yielded 30 g. BzOH and 2 g. benzonitrile, b10 68-72°. Equimolar quantities of MeCOEt, BzCl, and KCN treated as for I, the final reaction mixture **extracted** with Et2O, the **extract** washed with Na2CO3, dried, and **distilled** gave 40% II, b15175-80°. Alternatively equimolar amts. of redistd. MeCOEt cyanohydrin, BzCl, and tech. C5H5N heated 1 hr. at 100° cooled, the solid C5H5N.HCl separated by decantation of the liquid, the liquid washed, and **distilled** gave 35% II. Run 2. The pyrolysis of II was not studied in full detail, but sufficient evidence was obtained to demonstrate qualitatively the competiton between A1 and B2 scissions. **Distillation** of (a) gave a trace of MeCOEt, a main liquid fraction, b. 110-30°, which embraced the b.p. of CH2:CEtCN (VII) and MeCH:CMeCN (VII) (VII, b. 114°, VIII, b. 122°); this fraction was unsatd. and evolved NH3 when heated with **alkali**, all confirming the presence of olefinic nitriles. EtCOMe cyanohydrin and Ac2O warmed with a trace of concentrated H2SO4 and the cooled mixture shaken with brine, and the non-**aqueous** layer **distilled** gave 68% pure III, b13 92-4°, b. 198-9°. Runs 3-9. These runs gave qualitatively similar results. In each run, the products were worked up in 4 stages. The liquid (a) was **distilled**, the 1st volatile fraction was added to the liquid in the cold trap, and the HCN determined The presence of ketene was shown by the detection of acetanilide in the PhNH2 trap. The total free AcOH determined by titrating with a control experiment showed that olefinic nitriles did not interfere. The bulk of the AcOH was removed by shaking with brine and the insol. layer dried and fractionally **distilled**; the plot of the cumulative **distillative** volume against b.p. showed a plateau at 80°: fractions contained MeCOEt, VII, and VIII. The nitrile content was measured via the N content of those fractions. IV obtained in 65% yield as prisms, m. 51-2°. Pyrolysis 10. **Distillation** of (a) gave: 3.3 g., b. 70-96° consisting of C6H6 and cyclopentanone (IX); 0.8 g., b. 130-2°, containing IX; 23 g., b. 164-70°, yielded 78% 1-cyanocyclopentene which on **alkaline** hydrolysis gave 86% 1-cyclopentenecarboxylic acid; 1.6 g., b. 170-98°, and 36 g. residue which yielded 6% PhCN, and 84% BzOH. There was no unchanged IV. The **alkaline** trap contained 0.7% HCN. V was obtained in 70% yield as prisms, m. 73-4°. Pyrolyses 11-13. These runs gave similar results. Run 12 is typical. **Distillation** of (a) gave: 0.8 g., b. 80°, containing C6H6; 27 g., b. 84-170°, which redistd. gave 2 g., b. 156-7°, of cyclohexanone; 33 g., b. 170-220% which when redistd. gave 1.8 g., b. 190-5°, mainly PhCN and 25.5 g., b. 195-8° mainly 1-cyanocyclohexene; 27 g., b19 144-8°, BzOH; and 4.5 g. residual tar. The **alkali** trap contained about 0.1% HCN. VI, prepared in 20% yield in the same lines as IV and V as prisms, m. 72.5° (MeOH). Several variations failed to give yields comparable with those of IV and V. Pyrolysis 14. **Distillation** of (a) gave 0.3 g., b. about 80°, C6H6; 41 g., b. 176-225°, redistn. gave 20.9 g. containing cycloheptanone and PhCN, careful fractionation gave 8.6 g., b. 180-2°, mostly cycloheptanone and 7.5 g., b. 192-4° mostly PhCN, this fraction also gave about 58% 1-cyanocycloheptene, b. 213-14° converted by **alkaline** hydrolysis into 1-cycloheptenecarboxylic acid; 16.5 g., b5 118-20°, mostly BzOH, and 3 g. residual tar. There was no unchanged VI. The **alkaline** trap contained 0.3% HCN. Freshly redistd. com. CN2:CHCN was used, b.

78-9°. Pyrolysis 15. Preliminary runs in vessel P 2 showed the nitrile was very thermostable at 500-600°. At 650°, 20 g. of the nitrile gave 17.3 g. unchanged material plus 2.0 g. high boiling tars; an **alkali** trap removed 0.2% HCN and displaced N plus a little CH.tplbond.CH. A carboxylic ester may in principle follow at least 2 distinct thermal breakdown routes, A1 and B2, the balance being dictated by the presence or absence of some critical structural feature. The number and type of α-substituents in a Me ester have a critical bearing on the result. The reaction temperature itself influences the A1-B2 ratio. Although IV, V, and VI cannot yield HCN by the same route as does III, they did produce a slight trace of it on pyrolysis. Its origin is uncertain. A control experiment shows that CH2:CHCN does break down on pyrolysis but is not thermostable and the yield of HCN was only 0.2% at 650°. In the above cases the α-C atom of the alkyl group is fully substituted. When this is not so and the α-C atoms bear at least one H atom, simple competition between A1 and B2 scissions may be complicated by the appearance of 2 other concurrent competitive reactions. One of these will be described elsewhere.

CC 10E (Organic Chemistry: Benzene Derivatives)

IT Bonds
(carbon-O, breaking of, in esters)

IT Polyesters
(decomposition by heat)

IT 4111-08-4, Butyronitrile, 2-hydroxy-2-methyl-
(esters, preparation and pyrolysis of)

IT **126-98-7**, Methacrylonitrile
(formation in cyanoalkyl ester pyrolysis)

IT 502-42-1, Cycloheptanone
(formation in pyrolysis of 1-cyanocycloheptyl benzoate)

IT 1647-11-6, Butyronitrile, 2-methylene- 20068-02-4, Angelonitrile
(formation in pyrolysis of cyanoalkyl esters)

IT 74-90-8, Hydrocyanic acid
(formation of, in cyanoalkyl ester decompose by heat)

IT 65-85-0, Benzoic acid 67-64-1, Acetone 71-43-2, Benzene 463-51-4, Ketene
(formation of, in cyanoalkyl ester pyrolysis)

IT 108-94-1, Cyclohexanone
(formation of, in pyrolysis of 1-cyanocyclohexyl benzoate)

IT 120-92-3, Cyclopentanone
(formation of, in pyrolysis of 1-cyanocyclopentyl benzoate)

IT 64-19-7, Acetic acid 78-93-3, 2-Butanone 100-47-0, Benzonitrile
(formation of, in pyrolysis of cyanoalkyl esters)

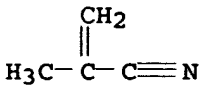
IT 32379-40-1, Cyclohexanecarbonitrile, 1-hydroxy-, benzoate 32379-42-3, Lactonitrile, 2-methyl-, benzoate 32379-43-4, Cyclopentanecarbonitrile, 1-hydroxy-, benzoate 106950-67-8, Cycloheptanecarbonitrile, 1-hydroxy-, benzoate
(preparation and pyrolysis of)

IT 636-82-8, 1-Cyclohexene-1-carboxylic acid 1560-11-8, 1-Cyclopentene-1-carboxylic acid 1855-63-6, 1-Cyclohexene-1-carbonitrile 3047-38-9, 1-Cyclopentene-1-carbonitrile 4321-25-9, 1-Cycloheptene-1-carboxylic acid 20343-19-5, 1-Cycloheptene-1-carbonitrile
(preparation of)

IT **126-98-7**, Methacrylonitrile
(formation in cyanoalkyl ester pyrolysis)

RN 126-98-7 HCAPLUS

CN 2-Propenenitrile, 2-methyl- (9CI) (CA INDEX NAME)



L36 ANSWER 35 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1958:97720 HCAPLUS
DN 52:97720
OREF 52:17170a-h
TI Aromatization of the Diels-Alder adduct of tetraphenylcyclopentadienone and fumaronitrile
AU Doering, Robert F.; Miner, Robert S., Jr.; Rothman, Leonard; Becker, Ernest I.
CS Polytech. Inst. of Brooklyn, Brooklyn, NY
SO Journal of Organic Chemistry (1958), 23, 520-2
CODEN: JOCEAH; ISSN: 0022-3263
DT Journal
LA Unavailable
AB Reaction of tetraphenylcyclopentadienone (I) and fumaronitrile (II) in PhBr gave trans-1,2-dihydrotetraphenyl-o-phthalonitrile (III). Br converted III to tetraphenyl-o-phthalonitrile (IV). **Alkali** dehydrocyanated III to 2,3,4,5-tetraphenylbenzonitrile (V). I (12 g.) and 2.8 g. II in 12 ml. PhBr refluxed 5.25 hrs., cooled to room temperature, and crystallized gave 10.09 g. III, m. 230-32° (C6H6) (**gas** evolved during melting). I and II directly formed IV without isolation of III (procedure A) or from III (procedure B). Procedure A. II (8.5 g.) and 38.4 g. I in 75 ml. PhBr refluxed until the effluent **gases** would no longer reduce a 0.02% solution of PdCl2 (about 2 hrs.), the mixture cooled, treated with 24 g. Br in 25 ml. PhBr, and refluxed 3 hrs. gave 13.4 g. IV, m. 265.3-5.4° (C6H6). Procedure B. A refluxing solution of 0.10 g. III in 2 ml. PhBr treated dropwise with 0.156 g. Br in 2 ml. PhBr, the mixture refluxed 3.5 hrs., the solution **distilled** to dryness, and the residue **extracted** with ligroine gave 0.050 g. IV. IV (1 g.) refluxed 12 hrs. with an excess of 10% alc. KOH gave tetraphenyl-o-phthalic anhydride, m. 289-90° (C6H6). I and CH2:CHCN refluxed in C6H6 or alone gave 7-oxo-1,4,5,6-tetraphenylbicyclo[2.2.1]hept-5-ene-2-carbonitrile (VI). I (1 g.) in 2.4 g. CH2:CHCN kept 4.5 hrs. during which time the red-purple color was discharged and cooled gave 0.63 g. VI, m. 204-6° (decomposition). VI (0.5 g.) in 3 ml. PhBr slowly heated to reflux (the color changed and there was no evidence of **gas** evolution), the mixture refluxed 5 hrs. with 3 ml. CH2:CHCN (the purple color discharged), and **distilled** gave 96% unchanged VI. VI on decarboxylation in either PhNO2 or in p-cymene gave similar results. The use of PhNO2 is described. Crude VI (2 g.) and 5 ml. CH2:CHCN in 90 ml. PhNO2 refluxed 10 hrs. at 165° gave 0.78 g. 2,3-dihydro-3,4,5,6-tetraphenylbenzonitrile (VII), m. 192.5-4.0° (C6H6-ligroine). VII (0.56 g.) and 0.4 g. Br in 30 ml. PhBr refluxed 6 hrs., the solvent **distilled**, and the residue recrystd. gave 0.49 g. V, m. 216-17° (alc.). A C6H6 solution of 0.197 g. III passed through a column of Merck Al2O3 gave 88% V. III heated 15 min. at 240-50° with **gas** evolution and cooled gave a poor yield of V. I (1.02 g.) and 0.0109 g. diethylenetriamine in 10 ml. PhBr refluxed 1 hr., the evolution of HBr detected by formation of a copious precipitate of AgBr, the solvent removed in vacuo, and the residue crystallized gave 0.95 g. V. All samples of V prepared above were identical. Tetracyclone (3 g.) and 1.48 g. propiolic acid in 10 ml. PhBr slowly heated, the color discharged within 10 min., and before 100° was reached, the solution refluxed 8 hrs., and the solvent removed gave 3.1 g.

2,3,4,5-tetraphenylbenzoic acid (VIII), m. 327.5-8.5° (Me2CO). V (0.38 g.), 1 g. KOH, 10 ml. alc., and 0.4 ml. **H2O** refluxed 12.25 hrs., the mixture digested 24 hrs. with 50 ml. more **H2O** on the steam bath, cooled, 10 ml. concentrated HCl added, and the mixture digested 4 hrs. gave 0.36 g. VIII. The yield of pure VIII was very low, however, and digesting 7 hrs. on the steam bath in 20 ml. alc. and 20 ml. 6N H2SO4 did not improve the purity. V (0.27 g.), 4.5 g. concentrated H2SO4, and 3.3 ml. **H2O** refluxed 12.25 hrs., diluted, filtered, washed, and recrystd. gave 5% VIII. Infrared spectra were superimposable.

CC 10E (Organic Chemistry: Benzene Derivatives)

IT Dehydrogenation
(of tetraphenylcyclohexadienecarbonitriles)

IT Diels-Alder reaction
(of tetraphenylcyclopentadienone, with acrylonitrile and fumaronitrile)

IT **107-13-1**, Acrylonitrile 764-42-1, Fumaronitrile
(Diels-Alder reaction with tetraphenylcyclopentadienone)

IT 103327-38-4, 1,3-Cyclohexadiene-1-carbonitrile, 2,3,4,5-tetraphenyl-
(preparation and dehydrogenation of)

IT 1181-03-9, Phthalonitrile, tetraphenyl- 3008-21-7, 5-Norbornene-2-carbonitrile, 7-oxo-1,4,5,6-tetraphenyl- 52316-18-4, Benzoic acid, 2,3,4,5-tetraphenyl- 78672-82-9, Benzonitrile, 2,3,4,5-tetraphenyl- 103266-79-1, 3,5-Cyclohexadiene-1,2-dicarbonitrile, 3,4,5,6-tetraphenyl-
(preparation of)

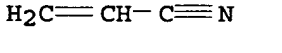
IT 479-33-4, Cyclopentadienone, tetraphenyl-
(reaction (Diels-Alder) with acrylonitrile and fumaronitrile)

IT 74-90-8, Hydrocyanic acid
(removal of, from 3,4,5,6-tetraphenyl-3,5-cyclohexadiene-1,2-dicarbonitrile)

IT **107-13-1**, Acrylonitrile
(Diels-Alder reaction with tetraphenylcyclopentadienone)

RN 107-13-1 HCAPLUS

CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 36 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1953:58498 HCAPLUS

DN 47:58498

OREF 47:9905i,9906a-i,9907a-i,9908a-b

TI Acrylonitrile as a starting material for synthesis of amino nitriles and polyamines

AU Kost, A. N.

SO Uchenye Zapiski Moskov. Gosudarst. Univ. im. M. V. Lomonosova (1950), (No. 131), 39-97

DT Journal

LA Unavailable

AB cf. C.A. 41, 1609h; 42, 3722g. Dissertation at the University (1946) with complete exptl. details and bibliography of 169 references. A laboratory preparation of CH2:CHCN (I) was developed as follows. To a hot saturated solution of 100 g. SnCl2 was added 30 g. Zn dust with stirring and, after completion of reaction, the mixture was allowed to stand 2 hrs., decanted, washed with 10% AcOH, let stand overnight with 60 ml. 80-90% AcOH, filtered, washed with **H2O** until neutral, and washed with EtOH and Et2O, giving 30-35 g. Sn dust. All traces of Zn must be removed for good results with this catalyst. Heating 50 g. HOCH2CH2CN with 5 g. of the above Sn dust in a **distillation** apparatus with chilled receiver so that **vapor** temperature is below 110° yields a 2-layer **distillate**; the upper layer

after drying with CaCl2 yields up to 90% I. If com. ethylene oxide is used in the preparation of the cyanohydrin, the product may be contaminated with MeCH:CHCN, **H2O**, and NH3; it is purified by 5-10 min. treatment with P2O5 and **distillation** (b758 78°). Refluxing the cyanohydrin with silica gel, activated C, MgSO4, Fe oxides, pieces of sheet Fe, Al foil, and Al2O3 gave but 0-30% yields of I. Passage of the cyanohydrin over Al2O3 at 200-20° gave but 18-20% I. To 950 ml. **aqueous** NH4OH (saturated in the cold) was added 95 g. I dropwise with cooling over 2 hrs. so that the mixture remained homogeneous; after 30 min. at room temperature, **distillation** gave 30% H2NCH2CH2CN, b14 77-8°, b23 89°, nD20 1.4390, d20 0.9584, which polymerized in several days in a sealed ampul even in darkness. **Distillation** of the higher-boiling residue gave 47% HN(CH2CH2CN)2, b14 177-9°, b22 209-11°, nD20 1.4630, d20 1.0196; HCl salt, m. 147-8° (from MeOH); N-Bz derivative, m. 112° (from MeOH). The free amine generated by addition of 50% **aqueous** Me2NH to solid NaOH was fed into 106 g. I with ice cooling over 6-8 hrs., and the mixture **distilled** after 2 hrs. at room temperature yielding 80-1% Me2NCH2CH2CN, b750 171°, nD20 1.4283, d20 0.8705; picrate, m. 151°; HCl salt, m. 199° (from MeOH). A mixture of 40 g. Et2NH and 26.5 g. I gave a slight heat evolution after 5-10 min.; refluxed on a steam bath 2 hrs. (yellow color) and **distilled**, it yielded 89-95% Et2NCH2CH2CN, b20 86-9°. If the heating is done in sealed tubes 6-8 hrs. no yellow color is formed and the yield is nearly 100%; the pure product b2 65°, b9 76°, b20 87°, b45 112°, b755 197.3° (corr.), d20 0.8761, nD20 1.4380; HCl salt, m. 120°; picrate, m. 85°. This (3.1 g.) refluxed 4 hrs. with 4. g. 25% NaOH and evaporated gave the amorphous Na salt of the corresponding acid; refluxing 5.3 g. of the nitrile with 11 g. concentrated HCl, cooling, filtering, and evaporating repeatedly in vacuo gave an amorphous mass, which was freed in **aqueous** solution of Cl ion by Ag2CO3, the Ag ion removed with H2S, and the filtrate evaporated, yielding 60% Et2NCH2CH2CO2H, m. 70-5°. The best reaction conditions for piperidine and I are as follows: Piperidine (17 g.) and 11.1 g. I mixed with cooling in an ampul (cooled until the heat evolution stopped in 15-20 min.) and heated 4 hrs. on a steam bath, then let stand overnight, gave 96-7% (CH2)5NCH2CH2CN, b18 114-15°; some 22% is formed by refluxing 5 g. piperidine with 5 g. HOCH2CH2CN 3 hrs. at 120-50°; if Sn dust is added the yield is 52.5%. An extensive study showed that the reaction of I with PhNHEt is best carried out by heating in an ampul 100 hrs. on steam bath in the presence of 3% Ac2O and a little hydroquinone, when 65-70% PhEtNCH2CH2CN, b8 158°, b11 164-5°, nD20 1.5503, d20 1.0260, is obtained; HCl salt, hygroscopic solid; picrate, oil; the free base couples with diazotized sulfanilic acid even in acid medium and the coupling product, isolated as the Na salt, is a green solid, giving a brown color in acid solution Coupling with diazotized p-O2NC6H4NH2 gave a brown product, C17H17O2N5, while tetrazotized benzidine reacts only slowly in acidified solution, yielding a red-violet solution which turns yellow in neutral or basic solution; the free azo derivative is soluble in organic solvents. Hydrolysis of PhEtNCH2CH2CN is very slow with **H2O** at 100° in a sealed tube; concentrated HCl at room temperature acts slowly and incompletely even in 48 hrs., while heating at 110-20° leads to loss of PhNHEt; heating with 30-40% H2SO4 gives an impure product. **Alkaline** hydrolysis gives low yields of the corresponding acid. Refluxing 14 g. PhEtNCH2CH2CN and 20 g. KOH in 20 ml. **H2O** and 70 ml. EtOH 15 hrs., acidifying with HCl, and repeatedly **extracting** with iso-BuOH, adding Et2O to the **extract** gave 33.1% PhEtNCH2CO2H.HCl, a high-melting solid, giving a brown color with FeCl3. This couples even in acid solution with diazotized sulfanilic acid, yielding a red azo derivative; p-O2NC6H4N2Cl also couples in acid medium, giving a red azo derivative PhEtNCH2CH2CN (4.5 g.) added slowly to 15 ml. concentrated H2SO4, and

the mixture let stand 40 hrs., then diluted with **H2O** (50 ml.), neutralized with concentrated NH4OH, and let stand overnight giving a precipitate of PhEtNCH2CH2CONH2, 68.5-76.5%, m. 55-8° (crude), m. 67° (from MeOH). I (35 g.) added to 20 g. dry (CH2NH2)2 dropwise with cooling at 15-20° over 2 hrs. the mixture shaken 2 hrs. at room temperature and let stand overnight in a stoppered flask gave 39.8% H2NCH2CH2NHCH2CH2CN, b1.5 101°, nD20 1.4727, d20 0.9912 (with MeZnI at room temperature only the primary amino group reacts, while at 100° all active H can be determined) (the picrate and styphnate are oils, while HCl salt is a viscous mass), and 59.8% (CH2NHCH2CH2CN)2, b1.5 174°, b3.5 191°, nD20 1.4793, d20 1.0256 [picrate and styphnate, oils; HCl salt, m. 184-7° (decomposition)]. The structure of the latter appears confirmed by the improbability of reaction of I with a cyanoethylated group, and further by the reaction with MeZnI which indicates 1.94 active H atoms/mole at 100° and 0.5 at room temperature Me2NCH2CH2CN treated with MeI in C6H6 with cooling gave the methiodide, m. 153° (from MeOH); EtI at room temperature yielded the ethiodide, m. 128.5° (from MeOH); EtBr at 60° yielded the ethobromide, m. 157° (from Et2O-MeOH); PrBr and CH2:CHCH2Cl at 80° yielded the corresponding quaternary salts, m. 189° (from Et2O-MeOH), and 185-7° (from MeOH), resp. Et2NCH2CH2CN with MeI at room temperature gave the methiodide, m. 152° (from MeOH), while EtI at 60° gave the ethiodide, m. 168° (from MeOH). (CH2)5NCH2CH2CN with MeI at 100° gave the methiodide, m. 152° (from MeOH), while EtI reacted slowly at 100° yielding the ethiodide, m. 160-1° (from MeOH).
Reduction of H2NCH2CH2CN with BuOH-Na gave variable yields when com. Na was used, because of traces of K (Dzirkal, C.A. 36, 2255.6); a 2% K-Na alloy gave high yields comparable to those obtained with pure Na. In the best procedure 30 g. of this alloy was rapidly treated with 14 g. H2NCH2CH2CN in 450 ml. BuOH, and despite vigorous reaction the mixture was immediately heated in an oil bath at 140-50°, cooled after 35-40 min., diluted with 130-50 ml. cold **H2O**, steam-**distilled** 4-6 hrs. into the calculated amount of **aqueous** HCl, and the **distillate** evaporated, yielding 81% CH2(CH2NH2)2.2HCl, m. 242° (from EtOH). Similar reduction of Me2NCH2CH2CN gave 52-6% Me2NCH2CH2 CH2NH2, b128-30 70-80° (crude), b20 44-5°, b748 133°, nD20 1.4415, d20 0.8272; di-HCl salt, m. 184° (from MeOH); picrate, C17H20N8O14, m. 211° (from **H2O**). The higher-boiling material yielded a little 3,3'-bis(dimethylamino)dipropylamine, b20 128-31°, nD20 1.4531 (HCl salt, hygroscopic solid; tripicrate, m. 200°; chloroplatinate, 2C10H25N3.3H2PtCl6, soluble in **H2O**, insol. in **aqueous** EtOH). Reduction of Et2NCH2CH2CN with NaBuOH gave 38-63% diamine; a 2% K-Na alloy gave good consistent 60-70% yields; pure Et2NCH2CH2CH2NH2, b12 61-2°, b70 85-7°, b80 99-100°, b755 168-70°, nD20 1.4435, gave 2 active H with MeZnI at room temperature and at 100°; picrate, m. 190.5° (from MeOH); Bz derivative, oil. Refluxing this amine with an equimolar amount of oleic acid 2 hrs., adding a little amine, heating another hr., concentrating, and evaporating with C6H6 gave a product that formed extremely stable organic-**aqueous** emulsions. The higher-boiling fractions from the above reduction gave a little bis(diethylamino) dipropylamine, b12 148-50° (picrate, m. 152°), also obtained if the reduction is run with pure Na.
Reduction of (CH2)5NCH2CH2CN with 2% K-Na in BuOH gave 57% 1-(3-aminopropyl)piperidine, b4 65-6°, b9 79-81°, nD20 1.4729. COCl2 with ROH gave the ClCO2R: R =Et, b752 92-4°; Pr, b742 114-16°, nD20 1.4036; iso-Pr, b745 101-2°, nD20 1.3996, d20 1.0777; Bu, b16 40-7°, b756 138°, nD20 1.4128, d20 1.0513. COCl2 with ROH in MePh in the presence of 5-8% quinoline gave the following ClCO2R: iso-Bu, b750 123-7°; iso-Am, b754 150-1°, nD20 1.4176, d20 1.0490; C8H17, b5 86.5°, b10 96-7°, b15

107°, nD20 1.4330, d20 0.9841; cyclohexyl, b25 80-5°, nD25 1.4628; 1-menthyl, b5 96°, b11 108-9°, nD20 1.4712; PhCH2, b7 85-7°; with an equimolar amount of quinoline were obtained: sec-Bu, 72%, b23 30-1°, b748 121-4°, nD20 1.4490; 1-methyl-2-cyclohexyl, b30 101.5°, nD20 1.4560; Ph, b7 64°, nD20 1.5162. The diamines (0.025 mole) in Et2O were treated with 0.025 mole powdered potash, then 1.5-2 ml. H2O, and RO2CCl in Et2O was added with cooling; the usual treatment gave the desired urethan derivs.: Me2NCH2CH2CH2NHCO2Et, 55.8%, b16 137-7°, nD20 1.4480, d20 0.9653; l-menthyl ester, 51.8%, b1 164.5°, nD20 1.4706, d20 0.9557, m. 45°; Et2NCH2CH2CH2NHCO2Et, 66.7%, b7 130°, nD20 1.4503; iso-Pr ester, 53.2%, b1.5 122-3°, nD30 1.4452, nD20 1.4493, d20 0.9367; sec-Bu ester, 42.5%, b5 132°, nD20 1.4513, d20 0.9334; C8H17 ester, 63.3%, b2 181.5-2°, nD30 1.4528, nD20 1.4577, d20 0.9168; cyclohexyl ester, 46.5%, b1.5 165-7°, nD30 1.4725, nD20 1.4752, d20 0.9765; 2-methylcyclohexyl ester, 81.5%, b2 177°, nD30 1.4693, nD20 1.4723, d20 0.9679; l-menthyl ester, 88.2%, b3 173°, nD20 1.4719, d20 0.9482, m. 31°; Ph ester, 33.6%, b3 196-201°, nD20 1.4770; PhCH2 ester, 24%, b3 132-5°, nD20 1.5030. C5H5NCH2CH2CH2NHCO2Et, 78.3%, b9 150-3°, nD20 1.4742, d20 1.0070; Pr ester, 70.4%, b18 187-8°, nD20 1.4735, d20 0.9935; iso-Pr ester, 62.8%, b8 155-8°, nD20 1.4706, d20 0.9878; Bu ester, 62.8%, b3 146°, b5 167-8°, nD20 1.4730, d20 0.9788; iso-Bu ester, 53.5%, b2 136.5-7°, nD20 1.4710, d20 0.9813; iso-Am ester, 66.2%, b2 159.5°, nD20 1.4712, d20 0.9749; C8H17 ester, 63.7%, b9 212-13°, nD20 1.4720, d20 0.9550.

CC 10 (Organic Chemistry)

IT Nitriles
(amino)

IT Amines
(preparation of)

IT Ammonium, (2-cyanoethyl)dimethylpropyl-, bromide
Ammonium, allyl(2-cyanoethyl)dimethyl-, chloride
Dipropylamine, 3,3'-bis(diethylamino)-, picrate
Piperidinium compounds, 1-(2-cyanoethyl)-1-ethyl-, iodide
Piperidinium compounds, 1-(2-cyanoethyl)-1-methyl-, iodide

IT Carbamic acid, (3-piperidinopropyl)-
(esters)

IT Ammonium, (2-cyanoethyl)ethyldimethyl-
(halides)

IT 148-87-8, Propionitrile, 3-N-ethylanilino- 3217-00-3, Propionitrile, 3,3'-(ethylenediimino)di- 22584-31-2, Propionitrile, 3-(2-aminoethylamino)-
(and derivs.)

IT 109-55-7, 1,3-Propanediamine, N,N-dimethyl- 1738-25-6, Propionitrile, 3-dimethylamino- 5351-04-2, Propionitrile, 3-diethylamino- 6711-48-4, Dipropylamine, 3,3'-bis(dimethylamino)-
(and salts)

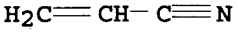
IT 92-87-5, Benzidine 100-01-6, Aniline, p-nitro- 121-57-3, Sulfanilic acid
(azo dyes from)

IT 82-71-3, Styphnic acid
(compds. with amines)

IT 78-92-2, sec-Butyl alcohol 108-93-0, Cyclohexanol 111-87-5, Octyl alcohol 123-51-3, Isopentyl alcohol 463-73-0, Formic acid, chloro- 583-59-5, Cyclohexanol, 2-methyl- 1490-04-6, Menthol 188309-01-5, Carbamic acid, (3-dimethylaminopropyl)- 679426-41-6, Carbamic acid, (3-diethylaminopropyl)-
(esters)

IT **107-13-1**, Acrylonitrile

(in preparation of amino nitriles and polyamines)
IT 104-78-9, 1,3-Propanediamine, N,N-diethyl- 111-94-4, Propionitrile, 3,3'-iminodi- 151-18-8, Propionitrile, 3-amino- 3088-41-3, 1-Piperidinepropionitrile 3232-12-0, Benzamide, N,N-bis(2-cyanoethyl)- 3529-08-6, Piperidine, 1-(3-aminopropyl)- 6050-28-8, Dipropylamine, 3,3'-bis(diethylamino)- 6972-41-4, β-Alanine, N,N-diethyl- 7505-16-0, 1,3-Propanediamine, N,N-diethyl-, picrate 10517-44-9, 1,3-Propanediamine, dihydrochloride 16688-98-5, Propionitrile, 3,3'-iminodi-, hydrochloride 42350-94-7, Ammonium, (2-cyanoethyl)trimethyl-, iodide 43151-55-9, Propionamide, 3-N-ethylanilino- 59837-08-0, β-Alanine, N-ethyl-N-phenyl-, hydrochloride 66999-80-2, Benzamide, N-(3-diethylaminopropyl)- 70709-64-7, β-Alanine, N,N-diethyl-, sodium salt 93115-66-3, Ammonium, (2-cyanoethyl)diethylmethyl-, iodide 93507-56-3, Ammonium, (2-cyanoethyl)triethyl-, iodide
(preparation of)
IT **107-13-1**, Acrylonitrile
(in preparation of amino nitriles and polyamines)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 37 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1952:23416 HCAPLUS
DN 46:23416
OREF 46:3976h-i,3977a-i,3978a
TI o-Quinones. II. The course of rearrangement of diazo ketones, o-quinonediazides, and acid azides
AU Horner, Leopold; Spietschka, E.; Gross, A.
CS Univ. Frankfurt a. M. Ger.
SO Ann. (1951), 573, 17-30
DT Journal
LA Unavailable
OS CASREACT 46:23416
GI For diagram(s), see printed CA Issue.
AB cf. C.A. 45, 4217e. The probable mechanism of rearrangement (and decomposition) of compds. of type R.C(:O)C(:N2)R' under the influence of ultraviolet light is outlined. The source of light was a "Labortauch" lamp S81 which was jacketed and could be cooled to 0° (or below). Ordinarily pure N was bubbled through (170 cc. of) the irradiated solution at low temps. BzC(:N2)Ph (I) (4.4 g.) irradiated in Et2O gave 3.5 g. Ph2C:C:O (identified as Ph2CHCONHPh, m. 180°). I (4.4 g.) irradiated in 165 cc. dioxane and 5 cc. **H2O** gave a good yield of Ph2CHCO2H, m. 145°, and in EtOH gave Ph2CHCO2Et, m. 57°. BzCH:N2 (II) irradiated in Et2O gave a polymer (C8H6O)x not melting at 260°, almost insol. in organic solvents, giving a red solution in H2SO4. Irradiated in **aqueous** dioxane, II gave PhCH2CO2H, m. 76°, and, in absolute alc., PhCH2CO2Et. When the irradiation was carried out in dioxane and PhNH2, PhCH2CONHPh, m. 116°, was formed. Irradiated with PhN:NPh (III) in C6H6, II gave PhCH.CO.NPh.NPh, m. 92°; similarly I and III in Et2O gave Ph2C.CO.NPh.NPh, m. 173° (cf. Cook and Jones, C.A. 35, 4765.1). 1,2-C6H4.CO.C(:N2).CH:CH (IV) in absolute alc. containing traces of HCl **gas**, when irradiated (under anhydrous conditions) until the coupling reaction with naphthol had ceased, gave 1,2-C6H4.CH(CO2Et).CH:CH, b16 160°; corresponding anilide, C16H13ON-, leaflets, m. 162° (from C6H6) (cf. Sus, C.A. 40, 5420.5, 5422.7). BzN3 irradiated in 100

cc. of an unidentified solvent at 6° gave about 87% PhNCO [identified by conversion into (PhNH)2CO, m. 232.5° (from alc.), the mother liquors from which gave BzNHPh, m. 165°]. To 50 cc. dry boiling xylene were added dropwise 10 g. IV in 100 cc. xylene, giving 6-7 g. of the dimeric indene ketene (V), m. 256° (from CHCl3 or AcOEt), and not the dinaphthalene dioxide structure ascribed to this product by Bamberger, et al. (C.A. 17, 2577). Hydrogenation in AcOEt with Raney Ni yielded the corresponding indan ketene, C20H16O2, yellow, m. 200-201°. V (5 g.) dissolved in 100 cc. hot glacial AcOH gave the compound (VI), colorless, m. 182-3°, giving a red enol reaction with FeCl3, a deep blue color with **alkali**, coupling with diazonium compds., and on hydrogenation adding 2 H2 to give the indan derivative, C20H18O3, m. 110° (decomposition) (from C6H6-petr. ether), whose Me ester (VII), viscous yellow oil, b5 220°. N2H4.**H2O** refluxed with VII in EtOH gave the monomeric hydrazide, C10H12ON2, m. 128°. Similarly HONH2 and VII yielded 1-indanhydroxamic acid, C10H11O2N, m. 170° (decomposition). ClC:CCl.CCl:CCl.CO.CO (VIII) (0.06 mole) and 0.02 mole I in 170 cc. Et2O were irradiated 1 hr., another 0.06 mole VIII then added, and finally another portion of VIII; the total irradiation period was 4 hrs. The product was the compound (IX), prisms, m. 187-8° (from CCl4). IX was also obtained, together with small amts. of tetrachloropyrocatechol, in 80% yield by refluxing VIII with Ph2C:CO in Et2O. Similarly prepared was the tetra-Br analog of IX, m. 218°. Heating (4.4 g.) IX 15 min. with 2 N **aqueous** NaOH and allowing to stand overnight gave 0.02 g. of an unidentified red compound, the filtrate from which, on acidification and Et2O **extraction**, yielded 1 g. of another unidentified substance. The Et2O **extract** on treatment with N2CH2 gave 2.2 g. tetrachloroveratrole, m. 88°, and from the mother liquors after refluxing with (solid) KOH, followed by addition of **H2O**, filtration, and acidification, was obtained 50 mg. Ph2C(OH)CO2H (m.p. not given). Me2CBrCOBr (under CO2) in Et2O was treated gradually with Zn turnings yielding Me2C:CO, which was **distilled** directly into VIII in Et2O and the mixture refluxed yielded the di-Me analog (X) of IX, C10H6O3Cl4, m. 148-9° (from Et2O), recovered unchanged from an **alkaline** solution by acidification. Practically no polymerization occurred when 20 cc. CH2:CHCN in C6H6 was mixed with I, II, or IV, followed by ultraviolet irradiation, and only traces of polyacrylonitrile (< 1%) were formed when CH2:CHCN was irradiated in C6H6 and BzN3 or in C6H6 (in a CO2 atmospheric) and PhN3.

CC 10 (Organic Chemistry)

IT Ketones
(diazo, rearrangement by ultraviolet light)

IT Rearrangements
(of diazo ketones, o-quinone diazides and acid azides)

IT Azides
(rearrangement of, by ultraviolet light)

IT Light, uv
(rearrangements of diazo ketones, quinone diazides and acid azides in)

IT Quinones
(o-)

IT 1-Indeneacetanilide
Indanketene, dimer
Indeneketene, dimer

IT Quinone diazides
(rearrangement of ortho, by ultraviolet light)

IT 103-71-9, Isocyanic acid, phenyl ester
(from BzN3)

IT 582-61-6, Benzoyl azide 879-15-2, 1(2H)-Naphthalenone, 2-diazo-
(irradiation with ultraviolet light)

IT 76-93-7, Benzilic acid 101-97-3, Acetic acid, phenyl-, ethyl ester

103-82-2, Acetic acid, phenyl- 117-34-0, Acetic acid, diphenyl- 525-06-4, Ketene, diphenyl- 621-06-7, Acetanilide, 2-phenyl- 944-61-6, Veratrole, 3,4,5,6-tetrachloro- 3468-99-3, Acetic acid, diphenyl-, ethyl ester 4695-14-1, Acetanilide, 2,2-diphenyl- 14383-98-3, 1,2-Diazetidin-3-one, 1,2,4-triphenyl- 60585-46-8, Dispiro[indene-1,1'-cyclobutane-3',1''-indene]-2',4'-dione 99067-94-4, 1-Indancarboxylic acid, hydrazide 101611-77-2, 1,2-Diazetidin-3-one, tetraphenyl- 170856-46-9, 1-Indeneacetic acid, ethyl ester 411210-42-9, Acetic acid, diphenyl(2,3,4,5-tetrachloro-6-hydroxyphenoxy)-, δ-lactone 854877-16-0, Dispiro[indan-1,1'-cyclobutane-3',1''-indan]-2',4'-dione 856810-42-9, Propionic acid, 2-methyl-2-(2,3,4,5-tetrachloro-6-hydroxyphenoxy)-, δ-lactone 857556-71-9, Acetic acid, diphenyl(2,3,4,5-tetrabromo-6-hydroxyphenoxy)-, δ-lactone 858225-56-6, 1-Indancarbohydroxamic acid 858225-96-4, 1-Indancarboxylic acid, 1-(1-indanylcarbonyl)- 858226-50-3, 1-Indancarboxylic acid, 1-(1-indanylcarbonyl)-, methyl ester 860358-30-1, 1-Indenecarboxylic acid, 1-(1-indenylcarbonyl)-
(preparation of)

IT **107-13-1**, Acrylonitrile
(reaction with diazo ketones and azides with ultraviolet irradiation)

IT 598-26-5, Ketene, dimethyl-
(reaction with tetrachloro-o-benzoquinone in ultraviolet light)

IT 2435-53-2, o-Benzoquinone, tetrachloro-
(reactions of, in ultraviolet light)

IT 622-37-7, Benzene, azido-
(reactions of, with acrylonitrile with ultraviolet irradiation)

IT 334-88-3, Methane, diazo-
(reactions of, with o-quinones)

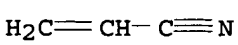
IT 3469-17-8, Acetophenone, 2-diazo-2-phenyl-
(rearrangement by ultraviolet light)

IT 3282-32-4, Acetophenone, 2-diazo-
(rearrangement of, by ultraviolet light)

IT **107-13-1**, Acrylonitrile
(reaction with diazo ketones and azides with ultraviolet irradiation)

RN 107-13-1 HCAPLUS

CN 2-Propenenitrile (9CI) (CA INDEX NAME)



L36 ANSWER 38 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN

AN 1951:11211 HCAPLUS

DN 45:11211

OREF 45:2005c-i

TI Meyer's synthesis of pyridines from acrylonitriles. Verification in the light of **Gastaldi**'s objections

AU Palit, Nirmalananda

CS Science Coll., Patna

SO J. Indian Chem. Soc. (1950), 27, 71-6

DT Journal

LA Unavailable

AB It is shown that the C6H6N structures assigned by Meyer (C.A. 3, 1747) are correct in general. An exception, 2,4-diphenyl-6-methylpyridine (I), noted by **Gastaldi** (C.A. 16, 2515, 2689), is probably confirmed. PhC(NH2):CHCN (2.8 g.), 5 g. PhC(OEt):CHBz, and absolute alc. added to alc. NaOEt (0.46 g. Na) and left 1 day give 2 g. 3-cyano-2,4,6-triphenylpyridine (II), m. 220° (from alc.) as reported by M. and I. II and fuming HCl, heated 4 h. in a sealed tube at 260° and

diluted with **H2O**, give 2,4,6-triphenylpyridine, m. 136-7°. m-H2NC6H4OH (2.5 g.), 5 g. PhCH:CHBz (III), and 40 mL. absolute alc. refluxed 7 h. with addition of a few drops alc. KOH, give 3 g. 7-hydroxy-2,4-diphenylquinoline (IV), m. 273° (from C6H6). To 3 g. IV in 450 mL. **aqueous** KOH (3 g. excess) on a **H2O** bath is added slowly (stirring) 9 g. tech. KMnO4 as a 5% solution, the excess KMnO4 decomposed with SO2, and the mixture filtered hot; by a tedious isolation and purification process, a poor yield of 2,4-diphenyl-5,6-pyridinedicarboxylic acid, m. 185° (from absolute alc.), is obtained. To 20 g. III, 14 g. CNCH2CO2Et (V), and 30 g. MeOH is added 5% MeOHNaOMe (VI) to **alkalinity** (all chems. must be very dry and pure), the mixture refluxed 2 h. with frequent 2-drop addns. of VI to keep **alkaline**, and left overnight; solvent removal, Et2O **extraction** of the residue, and Na2CO3 washing, drying, and evaporation of the Et2O give, on **distillation**, a few drops V, then 28 g. of a viscous mass (VII), b10 100-200°. VII in warm CCl4, saturated with dry HBr, left at 0°, and the mass rubbed with MeOH, gives 22 g. Et 2-keto-4,6-diphenyltetrahydro-3-pyridinecarboxylate (VIII), m. 160° (from alc.). Hydrolysis of VIII gives the acid. VII in hot AcOH is treated with Br, and the NH4Br filtered off; evaporation in vacuo leaves a residue which, dried over KOH, boiled with **H2O**, treated with hot **aqueous** NaOH (IX), and recrystd. repeatedly from alc. (Norit and kieselguhr), gives a low yield of Et 2-bromo-4,6-diphenyl-3-pyridinecarboxylate (X), m. 133-5°. IX gives some VIII. X (5 g.), 1 g. red P, and 12 mL. HI (d. 1.94) heated in a sealed tube 24 h. at 175-80° give crystals which, treated with boiling KOH and the solution concentrated and acidified, give an acid; this is refluxed 2 h. with powdered Ba(OH)2 and a little **H2O**, and the dried material (1 g.) gently heated (free flame) with Ba(OH)2, giving 0.5 g. **distillate** of 2,4-diphenylpyridine (XI), m. 68° (picrate, m. 189°) (cf. **Gastaldi**, loc. cit.). XI (1 g.) and 1.5 g. MeI refluxed 1 h. give the methiodide (XII), m. 206-8° (from alc.). XII (4 g.) is heated 2 h. in a sealed tube at 300-15°, dissolved in hot **H2O**, treated with concentrated NaOH, and steam-**distilled**; the Et2O-soluble portion of the residue gives, from ligroin, mainly XI (identified as the picrate). The ligroin filtrate gives, on evaporation, a few crystals of presumably I, m. 69-72° (from C6H6-ligroin); picrate, m. 212°, in agreement with G., loc. cit.

CC 10 (Organic Chemistry)

IT Ring closure or formation
(pyridine derivs. by)

IT 110-86-1, Pyridine
(derivs., from acrylonitriles)

IT **107-13-1**, Acrylonitrile
(derivs., pyridines from)

IT 580-35-8, Pyridine, 2,4,6-triphenyl- 1912-16-9, 2-Picoline, 4,6-diphenyl- 26274-35-1, Pyridine, 2,4-diphenyl- 26274-36-2, Pyridine, 2,4-diphenyl-, picrate 55249-89-3, Nicotinonitrile, 2,4,6-triphenyl- 107931-55-5, 7-Quinolinol, 2,4-diphenyl- 113926-73-1, 2-Picoline, 4,6-diphenyl-, picrate 846049-38-5, Nicotinic acid, 2-bromo-4,6-diphenyl-, ethyl ester 856963-09-2, Pyridinium, 1-methyl-2,4-diphenyl-, iodide 858474-69-8, Quinolinic acid, 4,6-diphenyl- 860233-48-3, 7-Quinolinol, 2,4-diphenyl-, picrate 860403-48-1, Nicotinic acid, tetrahydro-2-oxo-4,6-diphenyl-, ethyl ester
(preparation of)

IT **107-13-1**, Acrylonitrile
(derivs., pyridines from)

RN 107-13-1 HCAPLUS

CN 2-Propenenitrile (9CI) (CA INDEX NAME)

$H_2C{=}CH{-}C{\equiv}N$

L36 ANSWER 39 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1949:36515 HCAPLUS
DN 43:36515
OREF 43:6578e-i,6579a-f
TI Decarboxylation and cyclization reactions of some pimelic acid derivatives
AU Frank, Robert L.; McPherson, James B., Jr.
SO Journal of the American Chemical Society (1949), 71, 1387-91
CODEN: JACSAT; ISSN: 0002-7863
DT Journal
LA Unavailable
OS CASREACT 43:36515
AB MeC(:CH2)CAc(CH2CH2CN)2 (I), prepared in 35% yield from 98 g. pure mesityl oxide (II), 106 g. CH2:CHCN, 79 g. Me3COH, and 5 g. Triton B, m. 115-17° (cf. Bruson and Riener, C.A. 37, 1381.7). The purity of II was critical, com. II giving low yields. Saponification of 28.6 g. I with 20.8 g. KOH and 230 ml. **H2O** according to B. and R. gave 72% acid analog (III) of I, m. 137.5-8.5°; the haloform reaction with III in 20% NaOH with 9.5% NaOCl gave 67% MeC(:CH2)C(CO2H)(CH2CH2CO2H)2 (IV), m. 158-60°. Rearrangement of the propenyl group in IV: 46.7 g. IV and 1.51 g. BaCO3 intimately mixed and heated (3 batches, thermometer bulb in bottom of **distilling** flask) gave much **gas** at 285°, a temperature drop to 275°, and a rise to 320° with **distn** . of **H2O** and yellow oil, **extracted** with Et2O to give 12 g. 4-isopropylidenecyclohexanone (V), b1 54°, nD20 1.4817, d2020 0.959, MR calculated 41.1, MR found 41.2, cedarlike odor; semicarbazone, m. 196-8° (6 crystns. from EtOH); 2,4-dinitrophenylhydrazone, m. 130.5-2° (3 crystns. from MeOH and 7 from MeOH). Addition of 1320 cc. 4% O3 during 2.5 hrs. to 1.01 g. V in 15 cc. CH2Cl2 in a Dry-Ice bath, then dropwise addition at room temperature to 1.7 g. 30% H2O2, 0.1 cc. H2SO4, and 35 cc. **H2O**, keeping 45 min. at room temperature, refluxing 1 hr. (CH2Cl2 **vapor** contained no CH2O), then **distilling**, gave 24 cc. **H2O** containing a trace of CH2O and HCO2H, and giving a strong test for Me2CO (CHI3 and 2,4-dinitrophenylhydrazone). The **alkaline distillation** residue was **extracted** with Et2O, acidified, and saturated with (NH4)2SO4, precipitating a brown oil. CHCl3 **extraction** of the filtrate, concentration, and crystallization from 95% EtOH gave 1,4-cyclohexanedione, m. and mixed m. p. 77-8°. V (3.98 g.) in Et2O added slowly to MeMgI (from 15.6 g. MeI and 2.64 g. Mg) in anhydrous Et2O, then left 16 hrs. and added to 8 g. NH4Cl in ice and 125 g. **H2O**, HCl added to pH 6, and steam **distillation** of the Et2O **extract** gave 0.77 g. oil, b1 65°, crystallized on chilling to γ-terpineol, m. 63-7° (sublimed at 45-50° and 15 mm.), lilac odor. Confirmation of the possible decarboxylation of IV before cyclization to V was shown by heating 5 g. IV with 0.5 g. Cu-bronze powder to 195-205°, with formation of CO2 and 39% Me2C:C(CH2CH2CO2H)2 (Va), m. 104.5-6°. Dropwise addition of 0.596 mole I in 810 cc. dioxane (peroxide-free) to 2.68 moles NaOCl in 2300 cc. **H2O** and 850 cc. dioxane at 0-10°, addition after 4 hrs. at 0-10° of **aqueous** NaHSO3, washing with Et2O, acidification with concentrated HCl, filtration of the precipitate after 12 hrs., precipitation from 900 cc. hot **H2O** by chilling, and crystallization from CH2Cl2 gave 81% MeC(:CH2)C(CO2H)(CH2CH2CN)2 (VI), m. 166-7.5°. VI (45 g.), 4.5 g. Cu-bronze, and 4.5 g. powdered soft glass were heated under N to 200-30° with CO2 evolution, then cooled, the C6H6 **extract** washed with dilute H2SO4 and NaHCO3, Et2O added, and the filtrate

distilled to give 12.3 g. Me2C:C(CH2CH2CN)2 (VII), b1 135-7°, nD20 1.4733. The residue above, insol. in C6H6 and Et2O, was **extd** . with Me2CO, the filtrate concentrated, and the solid crystallized from dilute HCl and EtOH to give 26% α-(2-cyanoethyl)-α-isopropenylglutarimide (VIII), m. 119-21°, soluble in 5% NaOH, insol. in 5% NaHCO3; heating with Cu bronze to 350° gave no CO2, only a black tar. VII in boiling 2 N NaOH 6 hrs. gave Va. VII 2 g. in 25 cc. pure CCl4 at 0° was treated with 12 l. of 2.6% O3 during 1 hr., the solvent evaporated at 30° and 30 mm., 70 g. **H2O** and 2.85 g. Zn added, and 50 cc. **distilled** into 10 cc. **H2O** at 0°, giving no CH2O or HCO2H, but 17% Me2CO (2,4-dinitrophenylhydrazone). VIII heated just below the b. p. with N KOH 1 hr., the acidified solution concentrated to dryness, and crystallization from Me2CO gave 77% MeC(:CH2)C(CONH2)(CH2CH2CO2H)2, m. 164.5-6 °; boiling 3% **aqueous** KOH 16 hrs. or boiling H2SO4-HNO2 mixture (Cf. Haller and Bauer, C.A. 5, 3411) 1 hr. gave no hydrolysis. Dropwise addition of 16.3 g. VII in Et2O to gently refluxing PhNEtLi [prepared from 47.6 g. PhNHEt according to Ziegler, (C.A. 29, 746.4)] in Et2O during 5 hrs., addition to 360 cc. 2 N HCl, and Et2O **extraction** gave 13.8 g. crude 2-cyano derivative of V; 10% NaOH and 37 and 50% H2SO4 were without effect but refluxing with 10% H2SO4, steam **distillation**, 12 hrs.' more refluxing, and steam **distillation** gave hydrolysis and decarboxylation, V being isolated in low yield by Et2O **extraction** and identified as the 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 130-2° (from EtOH); semicarbazone, m. 193-5°, mixture with authentic derivative (m. 196-8°) m. 176-85°. The formation of the isomeric semicarbazone may indicate the presence of the isopropenyl analog of V. Infrared spectra did not differentiate between the Me2C and the MeC(:CH2) groups, both types of compds. showing maximum between 890 and 918 cm.-1.

CC 10 (Organic Chemistry)

IT Rearrangements
(of isopropenyl group)

IT Cyanoethylation
(of mesityl oxide)

IT Ring closure or formation
(of pimelic acid derivs.)

IT Spectra
(of γ-acetyl-γ-isopropenylpimelic acid and α-(2-cyanoethyl)-α-isopropenyl-glutarimide)

IT Isopropenyl group
(rearrangement of)

IT Carboxyl group
(removal of, from pimelic acid derivs.)

IT 16400-79-6, Heptanedinitrile, 4-acetyl-4-isopropenyl- 19620-36-1, Cyclohexanone, 4-isopropylidene-
(and derivs.)

IT 141-79-7, Mesityl oxide
(cyanoethylation of)

IT 111-16-0, Pimelic acid
(derivs.)

IT 586-81-2, γ-Terpineol 4379-08-2, 1,3,5-Pentanetricarboxylic acid, 3-isopropenyl- 26430-98-8, Heptanedioic acid, 4-isopropylidene- 412036-11-4, Heptanedioic acid, 4-acetyl-4-isopropenyl- 500302-78-3, Butyric acid, 4-cyano-2-(2-cyanoethyl)-2-isopropenyl- 500302-78-3, 3-Butenoic acid, 2,2-bis(2-cyanoethyl)-3-methyl- 688302-50-3, Aconitic acid, α-hydroxy- 854704-91-9, Glutarimide, 2-(2-cyanoethyl)-2-isopropenyl- 855895-60-2, Heptanedinitrile, 4-isopropylidene- 855896-79-6, Heptanedioic acid, 4-carbamoyl-4-isopropenyl-
(preparation of)

IT **107-13-1**, Acrylonitrile

(reaction with mesityl oxide)
IT **107-13-1**, Acrylonitrile
(reaction with mesityl oxide)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)

L36 ANSWER 40 OF 40 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1946:29318 HCAPLUS
DN 40:29318
OREF 40:5733h-i,5734a-h
TI Synthesis of monoalkyl-substituted diamines and their condensation products with 4,7-dichloroquinoline
AU Pearson, D. E.; Jones, W. H.; Cope, Arthur C.
CS Mass. Inst. Technol., Cambridge
SO Journal of the American Chemical Society (1946), 68, 1225-9
CODEN: JACSAT; ISSN: 0002-7863
DT Journal
LA Unavailable
AB Cyclohexanone (I) (25 g.) and 30 g. anhydrous C2H4(NH2)2, allowed to stand 1 h. and the mixture hydrogenated in 25 mL. absolute EtOH with Pt oxide at room temperature and an initial H pressure of 2 atmospheric for 12 h., give 83% of N-cyclohexylethylenediamine, b4 101-2°, nD25 1.4800, d425 0.9153 (all n and d. at 25°). Me2CO (116 g.), slowly added to cooled C2H4(NH2)2, the mixture allowed to stand overnight, and hydrogenated in 50 mL. absolute EtOH at 60° with 2 g. Pt oxide for 12 h., gives 50% of N-isopropylethylenediamine, b767 135.5-7.5°, n 1.4350, d. 0.8232. I (49 g.) and 90 g. (H2NCH2)2CHOH, mixed with cooling and the mixture reduced in 50 mL. absolute EtOH at 60° over Pt oxide (90% complete in 5 h., complete in 16 h.), give 77% of 1-cyclohexylamino-3-amino-2-propanol, b2 126-8°, m. 29-32°, n 1.4997, d. 1.0135; reduction in EtOH over Raney Ni at 160°/200 atmospheric for 12 h. gives 47%. CH2:CHCN (106.1 g.), added dropwise to 177.3 g. iso-PrNH2 at a temperature below 30° and the mixture stirred overnight at room temperature, give 95% of β-isopropylaminopropionitrile, b17 86-7°, n 1.4290, d. 0.8641; reduction of 190 g. over 20 g. Raney Ni at 100°/120 atmospheric gives 54% of N-isopropyltrimethylenediamine, b770 161-2°, n 1.4394, d. 0.8271. Iso-PrNH2 (45 g.) and 26.5 g. Na2CO3 in 300 mL. **H2O** and 50 mL. EtOH at 20-30°, treated dropwise with 60 g. Ac(CH2)3Cl (II), the mixture allowed to stand overnight, added rapidly to a mixture of 53 g. NH2OH.HCl and 30 cc. NaOH in 100 mL. **H2O** at 20-5°, allowed to stand overnight, and **extracted** with ether for 12 h., give 50% of 5-isopropylamino-2-pentanone oxime (III), pale yellow, b0.5 92-7°, m. 80.5-1.5°; iso-BuNH2 similarly gives 34% of the iso-Bu homolog (IV), m. 45-6°; tert-BuNH2 (20 g.) and 37.3 g. anhydrous K2CO3 at 50-60°, treated dropwise (1 h.) with 32.6 g. of II, 75 mL. C6H6 added, the bath heated to 90-5° during 4 h. and maintained at that temperature for 20 h., the C6H6 solution washed with 3 100-mL. portions of 3 N HCl, the acid exts. made alkaline with K2CO3 and reacted with NH2OH, give 11% of the tert-Bu homolog (V), m. 134-4.5°. III (0.1 mol) in 250 mL. BuOH, reduced with 23 g. Na (refluxing until all the Na is dissolved), gives 58% of 1-isopropylamino-4-aminopentane, b3 55-6°, n 1.4400, d. 0.8166; IV gives 61% of the iso-Bu homolog, b1 60-1°, n 1.4411, d. 0.8198; V yields 53% of the tert-Bu homolog, b13 84-7°, n 1.4398, d. 0.8178. 4,7-Dichloroquinoline (VI) (0.205 mol) and 0.20 mol of the diamine were heated at between 120-30° for 1-2

h. and then at 130-5° for an addnl. 2 h., giving 7-chloro-4-monoalkylaminoalkylaminoquinolines. VI (40.6 g.) and 12 g. C2H4(NH2)2 in 40 g. PhOH, heated 4 h. at 110-20°, the cooled product **extracted** with ether, the solid HCl salts added to 50 g. KOH in 300 mL. **H2O** and 400 mL. EtOH and shaken overnight, give 20 g. of 4,4'-(ethylenediimino)bis(7-chloroquinoline) (SN 14,725); crystallized from 800 mL. [CH2(OH)CH2]2O, the yield is 37%, m. 334.5-7° (decomposition); the alkaline filtrate yields 9 g. (21%) of 4-(2-aminoethylamino)-7-chloroquinoline (SN 14,724), m. 137-9°. 4-(Isopropylaminoethylamino) analog (SN 14,155), m. 129-30°, 52%; 4-(2-cyclohexylaminoethylamino) analog (SN 14,156), m. 151-1.5°, 48%; 4-(3-cyclohexylamino-2-hydroxypropylamino) analog (SN 14,689), m. 145.5-6°, 37%. 4-(3-Isopropylaminopropylamino) analog (SN 14,846), m. 107.5-8°, 51%. (H2NCH2)2CHOH (17.1 g.) and 39.6 g. VI with 20 g. PhOH, heated at 120-30° for 1 h., when the temperature of the reaction mixture suddenly rises to 175°, give 36% of 1,3-bis(7-chloro-4-quinolylamino)-2-propanol (SN 14,865), m. 143-5° and then 261-3° (decomposition); the 1:1 condensation product was not isolated. The 1-alkylamino-4-aminopentanes were added to about 25% of their weight of PhOH and a 2-3% mol. excess of VI and heated 4 h. at 150-60°; the products **distilled** at bath temps. of 180-200° as viscous yellow oils which solidified on standing. 4-(4-Isopropylamino-1-methylbutylamino)-7-chloroquinoline (SN 14,079), m. 103-5.5°, 48%; 4-(4-isobutylamino-1-methylbutylamino) homolog (SN 15,067), m. 72-4°, 28%; 4-(4-tert-butylamino-1-methylbutylamino) homolog, m. 117-17.5°, 49%.

CC 10 (Organic Chemistry)

IT Amines
(alkyl-substituted di-,reactions of, with chloro quinolines)

IT Ketones
(reactions of, with ethylenediamine)

IT 692-98-8, Propionitrile, β-isopropylamino- 3360-16-5, 1,3-Propanediamine, N-isopropyl- 5407-57-8, Quinoline, 4-(2-aminoethylamino)-7-chloro- 5418-54-2, Quinoline, 7-chloro-4-(3-isopropylaminopropylamino)- 5427-42-9, Quinoline, 7-chloro-4-(2-cyclohexylaminoethylamino)- 5700-53-8, Ethylenediamine, N-cyclohexyl- 6285-24-1, 2-Propanol, 1,3-bis(7-chloro-4-quinolylamino)- 19522-67-9, Ethylenediamine, N-isopropyl- 500533-57-3, Quinoline, 7-chloro-4-(2-isopropylaminoethylamino)- 500533-69-7, 2-Propanol, 1-(7-chloro-4-quinolylamino)-3-cyclohexylamino- 500533-69-7, Quinoline, 7-chloro-4-(3-cyclohexylamino-2-hydroxypropylamino)- 720685-07-4, 2-Pentanone, 5-tert-butylamino-, oxime 769951-95-3, Quinoline, 7-chloro-4-(4-isopropylamino-1-methylbutylamino)- 854901-22-7, 2-Propanol, 1-amino-3-cyclohexylamino- 855760-21-3, Quinoline, 4,4'-(ethylenediimino)bis[7-chloro- 858277-97-1, Quinoline, 4-(4-tert-butylamino-1-methylbutylamino)-7-chloro- 860544-42-9, 1,4-Pentanediamine, N1-isopropyl- 860544-44-1, 1,4-Pentanediamine, N1-isobutyl- 860546-22-1, 2-Pentanone, 5-isopropylamino-, oxime 860546-24-3, 2-Pentanone, 5-isobutylamino-, oxime 861014-94-0, 1,4-Pentanediamine, N1-tert-butyl-
(preparation of)

IT 67-64-1, Acetone
(reaction of, with ethylenediamine)

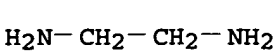
IT 75-64-9, tert-Butylamine 78-81-9, Isobutylamine
(reaction with 5-chloro-2-pentanone)

IT 86-98-6, Quinoline, 4,7-dichloro- 5891-21-4, 2-Pentanone, 5-chloro-
(reaction with amines)

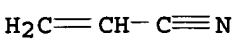
IT 108-94-1, Cyclohexanone
(reaction with diamines)

IT **107-15-3**, Ethylenediamine

(reaction with ketones)
IT 75-31-0, Isopropylamine 616-29-5, 2-Propanol, 1,3-diamino-
(reactions of)
IT **107-13-1**, Acrylonitrile
(reactions of, with isopropylamine)
IT **107-15-3**, Ethylenediamine
(reaction with ketones)
RN 107-15-3 HCAPLUS
CN 1,2-Ethanediamine (9CI) (CA INDEX NAME)



IT **107-13-1**, Acrylonitrile
(reactions of, with isopropylamine)
RN 107-13-1 HCAPLUS
CN 2-Propenenitrile (9CI) (CA INDEX NAME)



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